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A DETAILED COURSE

OF

QUALITATIVE CHEMICAL ANALYSIS

OF INORGANIC SUBSTANCES,

WITH

EXPLANATORY NOTES.

BY

ARTHUR A. NOYES, PH.D.,

PROFESSOR OF CHEMISTRY IN THE MASSACHUSETTS
INSTITUTE OF TECHNOLOGY.

THIRD REVISED AND ENLARGED EDITION.

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PREFACE.

SOME explanation of the origin and purpose of the present work is necessary. It arose out of the difficulty experienced in attempting to give a thorough course of qualitative analysis in limited time to large classes of students. The smaller text-books on the subject are too elementary in character to use in connection with such a course; they devote too little attention to the precautions to be observed to insure delicacy of the reactions, to the difficulties encountered by the student in actual work, and to the modifications of the process required in special cases. On the other hand, the manual of Fresenius, though complete and very valuable as a work of reference, is confusing to beginners on account of the complexity of its arrangement and insufficient explanation of the purposes of the various operations. The attempt has been made in the following pages to present an almost equally thorough scheme of qualitative analysis in a more concise and readily intelligible form.

The process of analysis here given was based originally on that of Fresenius, but it has undergone a number of important modifications suggested by experience with it in the laboratory. Among these may be specially mentioned the directions for the preparation of the substance for analysis and those for testing for acids, which have been made as distinct and definite as possible; for it is with these two parts of the process that the greatest difficulty is usually experienced. The methods of separation of the metals also differ somewhat from those of Fresenius, a different process being given for arsenic, antimony, and tin, and the choice between the two methods of analysis of the aluminum and iron groups being made to depend on a preliminary test for phosphates.

The most characteristic feature of the book, however, will be seen to be the method of presentation of the subject. Throughout the part devoted to the description of the process of analysis the matter is comprised under two distinct headings — the method of Procedure and the Notes upon it. The former consists exclusively of very detailed directions for carrying out the separations and special tests. The latter serve: first, to criticise the process and to point out the conditions to be fulfilled in order to insure delicacy of the tests; second, to show the purpose of each operation and reagent, where this is not sufficiently obvious; third, to explain abnormal results arising either from previous errors in the analysis or from the existence of conditions not provided for in the general scheme; and fourth, to suggest modifications of the process desirable in special cases. In the part devoted to the analysis for metals the description of each group is preceded by a brief tabular outline of the process, intended only to indicate the principles of the separation, not to serve as a working basis.

Besides this description of the process of analysis the book contains a separate part giving the Directions for Laboratory Work which have been used in connection with it. The author desires to express the opinion that the plan followed here and in the manual of Eliot and Storer of analyzing by the regular process solutions known to contain all the metals of each group is a far better preparation for the subsequent analysis of unknown substances than the more usual method of studying the reactions of each metal separately; for, however valuable the knowledge of the additional reactions involved in the latter method may be, it is found in practice that the performance of such a large number of independent tests in disconnected form makes but little impression on the mind of the student and causes confusion and loss of interest. Even where it is desired to teach the chemistry of the metals in connection with a course of qualitative analysis it is in the author's opinion better to do so as a supplement to the scheme of separation, in the form of additional reactions of the various metals. The laboratory work should be accompanied by lectures or recitations in which the process of analysis is taken up and discussed in detail.

In conclusion, the author desires to express his great indebtedness to Prof. T. M. Drown for his encouragement and valuable advice in regard to the general features of the book, and to Mr. W. S. Davenport, Instructor in Qualitative Analysis at the Institute, through whose cordial coöperation and numerous suggestions it has been greatly improved, not only in general character, but also in matters of detail.

PREFACE TO THE THIRD EDITION.

In this edition a number of changes suggested by recent investigations and by the continued use of the book in the laboratory have been made. In accordance with the researches of Fresenius, a much more delicate method of detection of the alkaline-earth metals has been introduced. The barium carbonate process in the presence of alkaline-earth phosphates has been simplified. The methods of detection of metals and acids in the dry way have been extended and more fully discussed; and practice with them has been introduced into the Directions for Laboratory Work. On the other hand, in the case of complete analyses, it is directed to confine the preliminary dry examination to the closed-tube test — a modification discussed on page 65. Finally, for the convenience of teachers, an appendix has been added showing the strength of reagents to be employed.

Objection has been raised to the system of instruction followed in this book on the ground that the omission of preliminary "reaction" work gives the student too narrow and limited an acquaintance with chemical facts. In reply to this objection, and especially in the interest of a reform of what the author believes to be a vicious method of instruction, the following remarks may be added to those which have been made on the subject in the preceding Preface. In the first place, it should be borne in mind that the introduction of an excessive amount of material is a common defect in modern education, and that the number of chemical facts involved in the systematic scheme of analysis is as great as can be properly assimilated by the student in the time usually devoted to the course. Secondly, it is to be considered that qualitative analysis is a satisfactory method of teaching a part of descriptive chemistry chiefly because it unites into a connected whole a great variety of isolated facts, and because it makes evident to the student a practical use of the information presented to him; but these advantages evidently do not apply to facts not directly related to the process of analysis. And thirdly, the additional knowledge which it is most desirable that the general student of descriptive chemistry should acquire when time permits, is not a more extended acquaintance with metathetical test-tube reactions, which involve for the most part merely questions of solubility, but rather a knowledge of new principles and new methods of manipulation — information that would be much better given by a course in inorganic preparations.

ARTHUR A. NOYES.

Boston, March, 1897.

PART I.

DIRECTIONS FOR LABORATORY WORK.

SEPARATION OF THE METALS INTO GROUPS.

1. As an example of the method of separation of the metals into groups, prepare a solution of $Pb(NO_3)_2$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, $Ca(NO_3)_2$, $Mg(NO_3)_2$, and KNO_3, by mixing together in a beaker about 5 cc. of each of these solutions. Add to it HCl little by little, as long as a precipitate continues to form (2 or 3 cc. at most); filter, and wash with cold water, till the washings (which should be added to the filtrate) are no longer acid to litmus paper. Heat the filtrate to boiling, and pass H_2S into it until it smells strongly of the gas, after removing it from the delivery tube, blowing away the gas collected on the surface, and shaking the liquid. Shake, heating at the same time; allow the precipitate to settle and filter; wash with hot water till free from acid, throwing the washings away. Add to the filtrate 10 cc. of NH_4Cl, NH_4OH till slightly alkaline, and colorless $(NH_4)_2S$, until the solution after shaking blackens a piece of filter paper moistened with lead acetate held above it. Heat and shake the solution till the precipitate settles quickly; filter, and wash with hot water containing a little $(NH_4)_2S$. Add $(NH_4)_2CO_3$ to the filtrate as long as a precipitate forms; filter, and wash the precipitate. To one portion of the filtrate add Na_2HPO_4. Evaporate the remainder of the filtrate nearly to dryness, and try the color imparted to the flame, using a platinum wire.

State in the note-book in the case of this and all subsequent experiments the reason of each operation and the purpose of the addition of each reagent. Write every reaction occurring in the process. Name the other metals which, if present, would be precipitated in this experiment by each of the group reagents. See page 15. Read the General Directions, pages 13–14.

2. As an example of the separation of the copper and tin groups, pass H_2S into a hot solution of $HgCl_2$ and $AsCl_3$ until the liquid is saturated. Filter, and wash the precipitate; warm some of it in a porcelain dish with 10 or 12 drops of (yellow) $(NH_4)_2S_x$ diluted with a little water; filter, and add HCl to the filtrate till slightly acid. For the sake of comparison, add HCl to 10 or 12 drops of pure $(NH_4)_2S_x$ diluted with water. (Read the notes on page 19.)

COPPER GROUP.

3. Prepare a solution of $Pb(NO_3)_2$, $AgNO_3$, and $HgNO_3$, using 10 cc. of each solution. Proceed with the separation as directed on pages 16 and 17.

4. In order to become familiar with the color and appearance of the various sulphides, add H_2S water to solutions of $PbCl_2$, $HgCl_2$, $BiCl_3$, $CdCl_2$, $Cu(NO_3)_2$, each taken separately, and previously acidified with a few drops of HCl. In the case of $HgCl_2$, try the effect of adding a *small* quantity of H_2S at first, then of adding an excess, shaking in each case.

5. Prepare a mixed solution of these five substances; dilute with water, and proceed according to pages 17–22, omitting the treatment with $(NH_4)_2S_x$ described on page 19.

TIN GROUP.

6. Pass H_2S into separate solutions of $AsCl_3$, $SbCl_3$, $SnCl_2$, and $SnCl_4$; also into a cold and then into a hot solution of Na_3AsO_4 acidified with HCl. Note the color and appearance of the precipitates.

7. Prepare a mixed solution of $AsCl_3$, $SbCl_3$, and $SnCl_2$, using 10 cc. of each. Dilute with 100 cc. of water; heat to boiling, and pass in H_2S till saturated. Filter, and proceed with the precipitate according to pages 24 and 25.

ALUMINUM AND IRON GROUPS.

8. *Ferrous and Ferric Salts.* — Add KCNS, $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ to separate portions of $FeSO_4$ solution.

9. Add the same reagents to separate portions of $FeCl_3$ solution. Contrast the results obtained in the two cases.

10. Try the following experiments illustrating methods of oxidizing ferrous to ferric salts, and read in this connection pages 27–29.

a. Boil 2 to 3 cc. of $FeSO_4$ solution with a small quantity of HNO_3.

b. Boil 2 to 3 cc. of $FeSO_4$ solution with an excess of bromine water.

c. Add HCl and a few crystals of $KClO_3$ to a little $FeSO_4$ solution, and heat.

In each of these three cases, dilute a portion of the solution thus obtained with water, and test it with $K_3Fe(CN)_6$ to see whether the iron has been completely oxidized. If this is found not to be the case, add more of the oxidizing agent to the remainder of the solution, and boil again.

11. Try the following experiments illustrating the reduction of ferric salts:

a. Pass H_2S into a solution of $FeCl_3$.

b. Add HCl and a piece of zinc to a little $FeCl_3$ solution in a test tube.

c. Add H_2SO_3 to a little $FeCl_3$ solution, and heat.

In each case continue the action till the solution is decolorized, and then test a portion with KCNS to show that complete reduction has taken place.

12. *Behavior towards General Reagents.* — To solutions of alum, chrome alum, $FeSO_4$, $FeCl_3$, $Zn(NO_3)_2$, $MnSO_4$, $NiSO_4$, and $Co(NO_3)_2$, each taken separately, add NH_4OH, first in small quantity, and then in moderate excess. To solutions of $FeSO_4$ and $MnSO_4$ add an equal volume of NH_4Cl, and then add NH_4OH.

13. Repeat the experiments, using NaOH in place of NH_4OH.

14. Add colorless $(NH_4)_2S$ in small quantity to solutions of the same substances.

15. *Separation in the Absence of Phosphates.* — Prepare a mixed solution of alum, $FeSO_4$, $Zn(NO_3)_2$, $MnSO_4$, $NiSO_4$, and $Co(NO_3)_2$, and analyze it as directed on pages 31-33 and 36–38.

16. *Experiments Illustrating the Behavior of Phosphates.* — Dissolve some $CaCO_3$ in dilute HCl, boil a few minutes to expel the CO_2, and add NH_4OH till alkaline. Note that no precipitate forms; then add $(NH_4)_2CO_3$.

17. Dissolve some $Ca_3(PO_4)_2$ in dilute HCl, add NH_4OH till alkaline; filter, and add $(NH_4)_2CO_3$ to the filtrate.

18. Dissolve another portion of $Ca_3(PO_4)_2$ in dilute HCl, add 10 to 15 cc. of $FeCl_3$ solution, add NH_4OH till alkaline; filter, and add $(NH_4)_2CO_3$ to the filtrate.

Explain fully the significance of these three experiments in the note-book. Read carefully pages 34 and 35 in this connection.

19. *Separation in the Presence of Phosphates.* — A solution containing the phosphates of barium, strontium, calcium, and magnesium, and salts of iron, chromium, aluminum, manganese, and zinc, will be found prepared in the laboratory. (Nickel and cobalt are omitted, since their separation is exactly the same as in the absence of phosphates.) Take 50 cc. of this solution, and proceed with it according to pages 29–30 and 40–43, omitting, however, the analysis of the alkaline-earth sulphates.

ALKALINE–EARTH GROUP.

20. Prepare a mixed solution of $BaCl_2$, $SrCl_2$, $Ca(NO_3)_2$, and $Mg(NO_3)_2$, and proceed with it according to pages 44–47.

ALKALI GROUP.

21. Add H_2PtCl_6 to separate solutions of KCl, NaCl, and NH_4Cl.

22. Warm a little solid NH_4Cl with CaO moistened with water; note the odor of the gas, and its action on red litmus paper.

ACIDS.

23. *General Tests.* — Add $BaCl_2$ to a solution of Na_2HPO_4, and to one of Na_2SO_4. Then add HCl. State in the note-book the other acids which, if present, react in the same manner as either of these. See pages 51 and 52.

24. Add $AgNO_3$ to separate solutions of K_2CrO_4, Na_2SO_4, Na_2HPO_4, $Na_2B_4O_7$, $(NH_4)_2C_2O_4$, Na_2CO_3, NaCl, KBr, KI, KCN, and Na_2S. Note the color of each precipitate. Then add HNO_3 to each in moderate quantity. See page 53.

25. *Special Tests.* — Try with the solid salts and solutions prepared for the purpose in the laboratory all the special tests for acids described on pages 55–64. Make the reduction tests for chromates with a small quantity of K_2CrO_4 solution, (1) by adding HCl and a lump of zinc, (2) by adding considerable strong HCl and boiling, (3) by acidifying with HCl and passing in H_2S.

DRY REACTIONS.

26. Heat in a closed tube, as described on page 66, each of the following substances: (1) $Ni(NO_3)_2.6H_2O$; (2) $KHC_4H_4O_6$; (3) HgO; (4) NH_4Cl; (5) FeS_2; (6) $KClO_3$; (7) $ZnSO_4$.

27. Try the test with concentrated H_2SO_4, described on page 70, with the following substances: (1) $KHC_4H_4O_6$; (2) KI; (3) KBr; (4) NH_4Cl; (5) $Na_2S_2O_3$; (6) KNO_3; (7) $NaC_2H_3O_2$.

28. Heat on charcoal, as described on page 68, the following substances: (1) $KClO_3$; (2) ZnO; (3) BiOCl; (4) PbS; (5) As_2O_3, (using a very small quantity); (6) $CuSO_4$.

29. Try the $NaPO_3$ bead test described on page 69, with: (1) MnO_2; (2)$FeSO_4$; (3) $Cr_2(SO_4)_3$; (4) ($CuSO_4$); (5) feldspar.

30. Try the flame test described on page 70, with: (1) Na_2SO_4; (2) K_2SO_4; (3) $CaSO_4$; (4) $SrSO_4$; (5) $BaSO_4$; (6) $CuSO_4$. Omit the moistening with H_2SO_4.

31. Examine with the spectroscope the salts provided for the purpose. Record the position on the scale of the characteristic lines of each element. Then analyze spectroscopically the unknown mixtures. See page 71.

UNKNOWN SUBSTANCES.

32. After completing the above preliminary work, ask for unknown substances for analysis. Test the solubility of the first five (or ten) substances in water and dilute HCl, and in addition apply to them only the dry tests described on pages 65–70, and report as far as possible the nature of their constituents. Make complete analyses of the remaining substances as follows: Note first the physical properties, make the closed tube test described on page 66, get the substance into solution (pages 72–80), and analyze the solution for metals according to pages 16–49. Prepare a solution for the analysis for acids (pages 81–83), and test for these according to pages 52–64. Describe the behavior of the substance through-

out the course of the analysis in the note-book. In reporting the results of the analysis of complex substances, do not simply enumerate the metals and acids found, but indicate the relative quantities of the various components, and state, if possible, the name of the substance. Compare its properties with the description of it given in the larger text-books in the library.

PART II.

THE PROCESS OF ANALYSIS.

GENERAL DIRECTIONS.

THE first aim of the student in analytical work should be to secure absolute certainty as to the correctness of his results; the next, to carry out the processes of analysis with rapidity. To attain these ends, the analyst must not only thoroughly understand in all their bearings the various operations which he performs, but he must also possess skill in manipulation. Thoughtless or unintelligent following of directions on the one hand, and lack of neatness or thoroughness in the performance of the operations on the other, are equally sources of error. The student will acquire the necessary knowledge by practice, if accompanied by a careful study of the principles of the process and by the habit of asking himself the purpose of each operation. The details of manipulation will be learned from practice and instruction in the laboratory. The following general directions, which apply throughout the whole scheme of analysis, should be always observed:

Precipitation. — In precipitating a solution always add the reagent gradually and only until a further addition produces no further precipitate. This can be determined in all cases by allowing the precipitate to settle, or by filtering a little of the liquid, and adding to the clear solution another drop of the reagent. In many cases, for example in precipitating with hydrogen sulphide, ammonia, or ammonium sulphide, it is more simply determined by the odor or color of the solution, since the reagent can impart its characteristic properties to the solution only when an excess of it has been added. By adding the reagent in this way, two important results are attained: first, it avoids an unnecessary excess of the reagent, by which the precipitate may be somewhat dissolved, the solution diluted, and subsequent tests made less delicate; and second, the precipitation is thus proved to be complete. This second result is so essential that any uncertainty in regard to it is entirely inadmissible. It is not enough for the analyst to believe that he has added the reagent in sufficient quantity to produce the desired result — he must conclusively prove that such is the case by adding more of it to the filtrate.

Washing Precipitates. — Always wash a precipitate until the wash water will no longer give a test for any substance known to be present in the filtrate. The object of precipitation being to separate one or more bodies from others in solution, it is obvious that this result is only incompletely attained, if the precipitate is not entirely freed from the liquid in which it was thrown down. For example, if the precipitate produced by hydrogen sulphide is not thoroughly washed, metals of the succeeding groups will be present in it, and will cause confusion and perhaps error by their unexpected appearance in the course of the analysis of the precipitate. Here, again, the analyst must not merely guess that the precipitate is thoroughly washed, he must invariably convince himself of it by making appropriate tests. If the filtrate contains free acid or alkali, it is done very simply by testing the wash water with litmus paper; if it contains chloride, by testing with silver nitrate, etc. On complete precipitation by the various reagents, and on proper washing of the precipitates, the success of an analysis very greatly depends.

Impurities in Reagents. — Bear constantly in mind that the substances to be tested for may be present in the reagents as impurities. In any case where this seems possible, make sure in regard to it by testing the reagent directly. The habit of thus making blank tests with reagents is an exceedingly important one to acquire; for the neglect of this precaution is often the cause of serious errors.

DETECTION OF THE METALS.

SEPARATION OF THE METALS INTO GROUPS.

Outline of the process.

<table>
<tr><td colspan="6">Solution containing all the metals: <i>add HCl.</i></td></tr>
<tr><td rowspan="4">Precipitate:
$AgCl$, $HgCl$,
$PbCl_2$.</td><td colspan="5">Filtrate: <i>add H_2S.</i></td></tr>
<tr><td colspan="2" rowspan="2">Precipitate:
HgS, PbS, Bi_2S_3, CdS, CuS, As_2S_3, Sb_2S_3, SnS, SnS_2. <i>Add $(NH_4)_2S_x$.</i></td><td colspan="3">Filtrate: <i>add NH_4OH and $(NH_4)_2S$.</i></td></tr>
<tr><td rowspan="2">Precipitate:
AlO_3H_3,
CrO_3H_3,
CoS, NiS,
FeS, ZnS,
MnS.</td><td colspan="2">Filtrate:
<i>add $(NH_4)_2CO_3$.</i></td></tr>
<tr><td>Residue:
HgS, PbS,
Bi_2S_3, CdS,
CuS.</td><td>Solution:
$(NH_4)_3AsS_4$,
$(NH_4)_3SbS_4$,
$(NH_4)_2SnS_3$.</td><td>Precipitate:
$BaCO_3$,
$SrCO_3$,
$CaCO_3$.</td><td>Filtrate:
Mg, K, and
Na salts.</td></tr>
</table>

Definition of the groups according to Fresenius.

GROUP I. *Alkali Group.* — Metals not precipitated by any of the general reagents: K, Na, NH_4.

GROUP II. *Alkaline-earth Group.* — Metals not precipitated by sulphides either in acid or alkaline solution, but precipitated by carbonates: Ba, Sr, Ca, Mg.

GROUP III. *Aluminum Group.* — Metals not precipitated by H_2S in acid solution, but precipitated by $(NH_4)_2S$ as hydrates: Al, Cr.

GROUP IV. *Iron Group.* — Metals not precipitated by H_2S in acid solution, but precipitated by $(NH_4)_2S$ as sulphides: Fe, Co, Ni, Mn, Zn.

GROUP V. *Copper Group.* — Metals precipitated by H_2S in acid solution, whose sulphides are insoluble in $(NH_4)_2S_x$: Ag, Pb, Hg, Bi, Cu, Cd.

GROUP VI. *Tin Group.* — Metals precipitated by H_2S in acid solution, whose sulphides are soluble in $(NH_4)_2S_x$: As, Sb, Sn, (Au, Pt).

PRECIPITATION AND SEPARATION OF LEAD, SILVER, AND MERCUROUS MERCURY.

Outline of the process.

<table>
<tr><td colspan="4">Precipitate: $AgCl$, $HgCl$, $PbCl_2$. *Add hot water.*</td></tr>
<tr><td colspan="2">Residue: $AgCl$, $HgCl$. *Add NH_4OH.*</td><td colspan="2">Solution: $PbCl_2$.</td></tr>
<tr><td rowspan="2">Residue:
$NH_2Hg\,Cl$
$+ Hg$,</td><td>Solution: *add HNO_3.*</td><td>*Add H_2SO_4 to one part.*</td><td>*Add H_2S to another.*</td></tr>
<tr><td>Precipitate: $AgCl$.</td><td>Precipitate:
$PbSO_4$.</td><td>Precipitate:
PbS.</td></tr>
</table>

Procedure. — Add to the cold solution dilute HCl little by little as long as the precipitate continues to increase; let it stand a few minutes; filter, and wash with a small quantity of cold water, adding the washings to the filtrate.

Notes. — 1. Non-formation of a precipitate proves absence of silver and mercurous mercury, but not of lead, as $PbCl_2$ is somewhat soluble in water. The more HCl added, the more complete will be the precipitation of the lead; for it, like most chlorides, is less soluble in dilute HCl than in water.

2. A great excess is to be avoided, as it interferes with the H_2S precipitation of the copper and tin groups.

3. Moreover, strong HCl dissolves all three of the chlorides quite readily.

4. If the solution is concentrated and strong HCl is added, certain chlorides soluble in water but less soluble in HCl may precipitate; for example, $BaCl_2$, NaCl, etc.

5. Dilute HCl may also precipitate BiOCl or SbOCl, but these dissolve readily on the addition of more HCl.

6. HCl may precipitate from a solution originally *alkaline* many other substances, namely, any substance held in solution by an alkaline solvent; for example, As_2S_3 from $(NH_4)_2S$ solution; AgCN or $Ni(CN)_2$ from KCN solution; silicic acid from sodium silicate; or metallic hydrates from solution in caustic alkalies. Such precipitates, if not dissolved by more HCl, must be treated according to the process used in preparing the solution of a substance for analysis.

Procedure. — Pour boiling water through the filter and test one portion of the filtrate with H_2SO_4, and another with H_2S. If lead is present, wash the precipitate with hot water till the wash water no longer reacts for lead. Then pour NH_4OH through the filter, and acidify the filtrate with HNO_3.

Notes. — 1. If the $PbCl_2$ is not completely washed out, it changes on addition of NH_4OH to a white basic salt, which passes through the filter and gives a turbid filtrate, which becomes clear, however, when HNO_3 is added.

2. AgCl unites with NH_4OH to form a soluble double compound, which is destroyed by HNO_3 with reprecipitation of AgCl.

3. The black residue on the filter is probably a mixture of NH_2HgCl and finely divided Hg:

$$2HgCl + 2NH_4OH = NH_2HgCl + Hg + NH_4Cl + 2H_2O.$$

PRECIPITATION OF THE COPPER AND TIN GROUPS.

Procedure. — Pass H_2S into the hot, slightly acid solution, until the odor of the gas is distinctly perceptible after shaking. Heat to boiling, allow the precipitate to settle, filter, and wash the precipitate with hot water till free from acid.

Dilute a small portion of the filtrate with two or three times its volume of water, and pass in more H_2S.

Notes. — 1. In addition to the sulphides of these groups a white precipitate of free sulphur is formed, if the solution contains any strong oxidizing agent; for example, nitric acid or a nitrate, a chlorate, a chromate, or a ferric salt. If a chromate is present, the solution changes in color from red to green; if a ferric salt, the solution becomes colorless.

2. It is useless to pass H_2S into a solution containing much HNO_3 or aqua regia. If, therefore, these acids have been used in dissolving the substance, the solution should be evaporated almost to dryness and the residue dissolved in water and a little HCl, before passing in H_2S.

3. The solution must be slightly acid to prevent the precipitation of Zn, Co, and Ni; but too much acid prevents the precipitation of the metals of the copper and tin groups, especially of cadmium, lead, antimony, and tin. One part of acid (1.12 sp. gr.) to 20 or 25 of water is a suitable concentration. If much more dilute than this, some zinc will be precipitated.

4. Complete precipitation may fail from two causes: use of an insufficient quantity of H_2S or presence of too much HCl. Therefore always test the filtrate by passing more H_2S and by further dilution.

5. Dilution with water before passing H_2S may cause precipitation of BiOCl or SbOCl. It is not necessary nor advisable to redissolve these precipitates by addition of more HCl; for H_2S changes them readily to sulphides.

6. Arsenic, in the higher state of oxidation, is precipitated by H_2S very slowly indeed in the cold, and not very rapidly, hot. The precipitate is As_2S_5: $2H_3AsO_4 + 5H_2S = As_2S_5 + 8H_2O$. The slow formation of a yellow precipitate is therefore a strong indication of arsenic, and when it occurs the solution should be kept nearly boiling during precipitation.

7. *Colors of the Sulphides.* — Black or brownish black: Ag_2S, HgS, PbS, Bi_2S_3, CuS, SnS. Yellow: CdS, As_2S_3, As_2S_5, SnS_2. Orange: Sb_2S_3, Sb_2S_5. Mercuric salts give at first a white precipitate consisting of a double compound ($HgCl_2.2HgS$), which turns yellow, red, and finally black with more H_2S, owing to conversion to HgS. Lead salts give a

red precipitate of analogous composition when precipitated by H_2S from a solution containing considerable HCl.

SEPARATION OF THE COPPER AND TIN GROUPS.

Procedure. — Warm a portion of the H_2S precipitate, or the whole of it, if small in amount, with ten or twelve drops of yellow $(NH_4)_2S_x$ diluted with a little water. Filter, and add HCl to the filtrate till it reacts acid with litmus paper. If the precipitate which forms is colored yellowish or orange, treat the remainder of the H_2S precipitate in the same way, using rather more $(NH_4)_2S_x$, and repeating the treatment with successive portions of it till the filtrate from the last treatment is precipitated white by HCl. Wash the residue insoluble in $(NH_4)_2S_x$ with water till the wash water no longer reacts alkaline. Collect on a filter the precipitate obtained by the addition of HCl to the $(NH_4)_2S_x$ solution, wash it once or twice with water, and dry it as much as possible by suction.

Notes. — 1. If the H_2S precipitate has not been thoroughly washed, the $(NH_4)_2S_x$ will precipitate metals of the aluminum and iron groups contained in the solution adhering to it, and these will appear in the separation of the copper group.

2. Yellow ammonium sulphide must be used, for the colorless does not dissolve SnS. A pure white precipitate after neutralization with HCl is taken as proof of the absence of As, Sb, and Sn, hence the use of very little $(NH_4)_2S_x$ at first; for, otherwise, the large amount of separated S would conceal the color of small quantities of As_2S_5, Sb_2S_5, and SnS_2.

3. The sulphides dissolve in $(NH_4)_2S_x$ with formation of salts of sulpho-acids:

$$As_2S_3 + 3(NH_4)_2S_x = 2(NH_4)_3AsS_4 + (3x - 5)S.$$
$$Sb_2S_3 + 3(NH_4)_2S_x = 2(NH_4)_3SbS_4 + (3x - 5)S.$$
$$SnS + (NH_4)_2S_x = (NH_4)_2SnS_3 + (x - 2)S.$$

4. When HCl is added to these compounds, the *higher* sulphides are precipitated, for example:

$$(NH_4)_2SnS_3 + 2HCl = SnS_2 + 2NH_4Cl + H_2S.$$

5. CuS dissolves somewhat in $(NH_4)_2S_x$, but much less in Na_2S_x. HgS dissolves readily in Na_2S_x, but not in $(NH_4)_2S_x$. Hence, when the preliminary examination or the color of the solution indicates Cu, and there is no reason to suspect Hg, use Na_2S_x.

6. When Cu is present, and $(NH_4)_2S_x$ is used, a liver-colored precipitate is obtained on neutralizing with HCl.

SEPARATION OF MERCURY, LEAD, BISMUTH, CADMIUM, AND COPPER.

Outline of the process.

<table>
<tr><td colspan="5">Precipitate: HgS, PbS, Bi_2S_3, CdS, CuS. Boil with HNO_3.</td></tr>
<tr><td rowspan="3">Residue: HgS.
Dissolve in HCl and $KClO_3$; add $SnCl_2$.</td><td colspan="4">Solution: add H_2SO_4.</td></tr>
<tr><td rowspan="4">Precipitate:
$PbSO_4$.</td><td colspan="3">Filtrate: add NH_4OH.</td></tr>
<tr><td rowspan="2">Precipitate:
BiO_3H_3.
Dissolve in HCl, and add to H_2O.</td><td colspan="2">Filtrate: add KCN and H_2S.</td></tr>
<tr><td rowspan="2">Precipitate: $HgCl$.</td><td rowspan="2">Precipitate:
CdS.</td><td rowspan="2">Solution:
$KCN.CuCN$.</td></tr>
<tr><td>Precipitate:
$BiOCl$.</td></tr>
</table>

Procedure.—Boil the residue from the $(NH_4)_2S_x$ treatment in a porcelain dish with dilute HNO_3 (1 part of acid 1.2 spec. grav., and 3 of water) for ten minutes, or until dissolved, replacing the acid which evaporates. Filter and wash.

Notes.—1. HgS remains undissolved; the other sulphides dissolve. The reactions are: $3PbS + 8HNO_3 = 3Pb(NO_3)_2 + 3S + 2NO + 4H_2O$, etc.

2. A black residue is not necessarily HgS, but may be S with PbS, CuS, or Bi_2S_3 inclosed in it. The confirmatory test for Hg should therefore always be tried.

3. Continued action of strong HNO_3 converts HgS to $Hg(NO_3)_2 2HgS$, a white insoluble compound. A heavy white or yellow residue should therefore be tested for Hg.

4. Dilute HNO_3 oxidizes PbS partly, and strong HNO_3 oxidizes it almost entirely to $PbSO_4$: $3PbS + 8HNO_3 = 3PbSO_4 + 8NO + 4H_2O$. The insoluble residue may therefore contain $PbSO_4$ as well as HgS; but owing to the solubility of $PbSO_4$ in HNO_3, some Pb will always pass into the filtrate.

5. The insoluble residue may also contain oxides of tin and antimony, especially the former, if the $(NH_4)_2S_x$ treatment has been insufficient.

Procedure. — To confirm the presence of Hg, dissolve the residue by heating with HCl and a small crystal of $KClO_3$. Boil to expel the excess of chlorine, and add a little $SnCl_2$ solution.

Notes. — 1. If the excess of chlorine is not expelled before adding $SnCl_2$, the reduction of the $HgCl_2$ is prevented.

2. The reaction between $KClO_3$ and HCl is approximately as follows:

$$2KClO_3 + 4HCl = 2KCl + Cl_2 + 2ClO_2 + 2H_2O.$$

Procedure. — To the filtrate from the HgS add about 5 cc. of strong H_2SO_4, and evaporate in a porcelain dish till the white fumes of H_2SO_4 come off thickly. After *cooling* add about 50 cc. of water and pour into a beaker; note whether the solution is at all turbid, and if so, filter it.

Notes. — 1. $PbSO_4$ is slightly soluble in HNO_3; hence the need of expelling it.

2. $PbSO_4$ is slightly soluble in *concentrated* H_2SO_4; hence the dilution before filtering.

3. $PbSO_4$ is less soluble in *dilute* H_2SO_4 than in H_2O; it is therefore advantageous to have the acid present in slight excess.

4. Ammonium salts, for example NH_4NO_3, also dissolve $PbSO_4$; hence the need of thoroughly washing out the $(NH_4)_2S_x$ before dissolving the H_2S precipitate in HNO_3.

5. A very minute precipitate of $PbSO_4$ not otherwise noticeable may be detected by giving a rotary motion to the beaker, thus causing the precipitate to collect in the center.

Procedure. — To the filtrate from the $PbSO_4$ add NH_4OH till alkaline, and then, if a precipitate forms, a small quantity more, in order to redissolve CdO_2H_2 and CuO_2H_2. Heat gently, filter, and wash the precipitate. Dissolve it by pouring a little strong HCl through the filter; evaporate the solution to one or two drops, and pour into a beaker of water.

Notes. — 1. If the H_2S precipitate has been insufficiently washed, AlO_3H_3, FeO_3H_3, etc., may precipitate on the addition of NH_4OH.

2. If the lead has not been completely removed by close adherence to the above directions, it also will precipitate at this point.

3. The formation of a precipitate by NH_4OH must therefore never be taken as proof of the presence of Bi, but the confirmatory test must always be tried.

4. Reaction: $BiCl_3 + H_2O = BiOCl + 2HCl$.

5. The more completely the HCl is removed by evaporation, the more delicate will be the test for Bi. Time is sometimes required for the precipitation of the BiOCl.

6. Sb and Sn salts like those of Bi are precipitated by H_2O, but these should not be present in the solution at this stage of the analysis. Tartaric acid prevents the precipitation of Sb salts by H_2O, but not that of Bi or Sn salts.

Procedure. — Unless distinctly blue, test a small portion of the filtrate from the BiO_3H_3 for Cu by acidifying with acetic acid and adding $K_4Fe(CN)_6$. If the ammoniacal solution is blue, add KCN little by little till the blue color due to the Cu is completely discharged, and then pass in H_2S for a few seconds.

Notes. — 1. Cd is also precipitated by $K_4Fe(CN)_6$; but the precipitate is white.

2. The precipitation with $K_4Fe(CN)_6$ is a more delicate test for Cu than the blue coloration with NH_4OH.

3. A potassium cupr*ous* cyanide (KCN.CuCN) is formed by the action of the KCN, and this compound is not decomposed by H_2S. Cd forms with excess of KCN the double salt $2KCN.Cd(CN)_2$, which is decomposed by H_2S.

4. A yellow coloration with H_2S does not indicate Cd. A yellow precipitate must be obtained.

5. A black precipitate (due to HgS, PbS, FeS, etc.,) is sometimes obtained in testing for Cd with H_2S, owing to some previous error in the analysis. To determine whether Cd is present in it, filter it off, wash it, and boil it several minutes with an excess of dilute H_2SO_4 (one part of acid to four of water); filter, dilute the filtrate, and saturate it with H_2S. H_2SO_4 of this strength dissolves CdS, changes PbS to insoluble $PbSO_4$, but does not affect CuS or HgS.

ADDITIONAL REACTIONS OF METALS OF THE COPPER GROUP.

1. ***Behavior towards the Alkalies.*** — All metals of this group are precipitated both by NaOH and NH_4OH. Excess of NaOH dissolves only the Pb precipitate. Excess of NH_4OH dissolves Ag_2O, CdO_2H_2, and CuO_2H_2. The precipitates are hydroxides in the case of Bi, Cd, and Cu, the oxide in the case of Ag, and basic salts in the case of Pb. Hg gives with NaOH, Hg_2O (black) and HgO (yellow); while with NH_4OH substituted ammonium compounds are formed, *e.g.*, $NH_2Hg_2NO_3$ and NH_2HgCl.

2. *Mercurous and Mercuric Salts.* — These are distinguished (1) by HCl, which precipitates the former and not the latter; (2) by NH_4OH, which gives a black precipitate with the former and a white one with the latter. The reactions are:

$$2HgNO_3 + 2NH_4OH = NH_2Hg_2NO_3 + NH_4NO_3 + 2H_2O.$$
$$HgCl_2 + 2NH_4OH = NH_2HgCl + NH_4Cl + 2H_2O.$$

SEPARATION OF ARSENIC, ANTIMONY, AND TIN.

Outline of the process.

<table>
<tr><td colspan="4">Precipitate: As_2S_5, Sb_2S_5, SnS_2. <i>Add strong HCl.</i></td></tr>
<tr><td rowspan="2">Residue: As_2S_5.
<i>Dissolve in HCl and $KClO_3$; add NH_4OH, NH_4Cl, and $MgCl_2$.</i></td><td colspan="3">Solution: $SbCl_3$, $SnCl_4$, (and small amount of H_3AsO_4). <i>Place in hydrogen generator.</i></td></tr>
<tr><td rowspan="2">Residue: Sn.
<i>Dissolve in strong HCl and add $HgCl_2$.</i></td><td colspan="2">Gas evolved: SbH_3 (and AsH_3).
<i>Pass through a hot tube.</i></td></tr>
<tr><td rowspan="2">Precipitate:
$MgNH_4AsO_4$.</td><td colspan="2">Deposit: Sb (and As).
<i>Treat with NaOCl.</i></td></tr>
<tr><td>Precipitate:
HgCl.</td><td>Residue:
Sb.</td><td>Solution:
(H_3AsO_4).</td></tr>
</table>

Procedure. — Heat gently (not to boiling) the precipitated sulphides, dried as much as possible by suction, with strong HCl (1.2 spec. grav.) as long as the vapors blacken paper moistened with $Pb(C_2H_3O_2)_2$ and NH_4OH. Dilute with a little water, filter, and wash the undissolved residue. Dissolve it in a little HCl with addition of a crystal (or two) of $KClO_3$, heat to expel the excess of chlorine, add NH_4OH till alkaline, filter if turbid, and then add enough more NH_4OH to form one third the volume of the solution; add magnesia mixture, stir, and if no precipitate forms at once, allow it to stand over night.

Notes. — 1. The separation of As_2S_5, Sb_2S_5, and SnS_2 by HCl is not perfect. Some Sb_2S_5 and SnS_2 may remain undissolved, and small quantities of arsenic pass into solution. It is to prevent the latter as far as possible that the acid is only warmed, not boiled.

2. In case there is reason to believe that the precipitate consists mainly of As_2S_5, warm it first with a saturated solution of $(NH_4)_2CO_3$ (made by dissolving the finely ground solid

salt in cold water), filter, treat the precipitate with strong HCl as above directed, and acidify the $(NH_4)_2CO_3$ filtrate with HCl. $(NH_4)_2CO_3$ dissolves As_2S_5 without difficulty, but dissolves Sb_2S_5 and SnS_2 only slightly.

3. If a yellow turbidity (Sb_2S_3 or SnS_2) appears on diluting the HCl solution with water, it shows that the H_2S has not been completely expelled.

4. On the addition of NH_4OH any antimony or tin not dissolved out of the mixed sulphides by the strong HCl will be precipitated as hydrate.

5. $MgNH_4AsO_4$ like $MgNH_4PO_4$ is somewhat soluble in water, but much less so in NH_4OH. Hence the solution should be concentrated and an excess of NH_4OH added. The precipitate is crystalline, and adheres to the sides of the vessel, especially along the lines rubbed with the glass rod.

6. REACTIONS:

$$As_2S_5 + 10Cl + 8H_2O = 2H_3AsO_4 + 5S + 10HCl.$$
$$H_3AsO_4 + 3NH_4OH = (NH_4)_3AsO_4 + 3H_2O.$$
$$(NH_4)_3AsO_4 + MgCl_2 = MgNH_4AsO_4 + 2NH_4Cl.$$

Procedure. — Place a piece of platinum and some zinc in a flask fitted with a thistle and delivery tube, and add some dilute HCl. Cause the gas to pass through a tube containing dry $CaCl_2$, and then through a hard glass tube drawn to a capillary at the end and at two intermediate points. After the air has been expelled (proved by collecting some of the gas in a small test tube and igniting it), light the gas at the end of the apparatus, and heat the hard glass tube just back of the first capillary with a small Bunsen flame. Continue this for a few minutes to see that no mirror forms; then pour in the solution of $SbCl_3$ and $SnCl_4$ *little by little.* Note whether any deposit forms in the capillary, and whether the platinum in the generator becomes blackened. After some minutes pour out the liquid in the generator, wash the residue by decantation with water, boil with strong HCl till entirely dissolved, dilute the solution, and add $HgCl_2$. Break off the hard glass tube just beyond the mirror, and immerse it in a test tube containing NaOCl solution. Note whether the mirror dissolves wholly or in part.

Notes. — 1. $SnCl_4$ is reduced by nascent hydrogen to metallic tin, which deposits on the zinc. A part only of the Sb deposits on the platinum, the remainder being further reduced to SbH_3. The H_3AsO_4 is reduced to AsH_3 without precipitation of arsenic.

2. Heat decomposes SbH_3 and AsH_3 into antimony or arsenic and hydrogen.

3. As small quantities of As_2S_5 are dissolved by strong HCl, a deposit in the capillary, unless accompanied by distinct blackening of the platinum, must not be considered proof of the presence of Sb. The test with NaOCl removes all doubt, however; for an arsenic mirror dissolves almost instantly, forming H_3AsO_4, while antimony remains unaffected for a long time. Even when the deposit consists of both metals, it is easy to detect the presence of both; for arsenic, being more volatile, deposits in the part of the capillary more remote from the flame, and this part of the mirror is seen to dissolve completely on treatment with NaOCl. This reagent serves therefore not only to confirm the presence of antimony but also to detect traces of arsenic so small as not to be shown by the test with $MgCl_2$ and NH_4Cl.

4. The presence of an element may be established in three ways: (1) by isolation of the element itself; (2) by formation of one of its characteristic compounds; (3) by causing a change to take place in some other substance. The test for tin with $HgCl_2$ is one of the few examples of the last method.

ADDITIONAL REACTIONS OF METALS OF THE TIN GROUP.

1. Arsenic and antimony may be detected in the original solution, even while other metals are present, by the generator test above described; and where minute quantities are to be detected, that test should be employed, since the color of their sulphides may be concealed by the sulphur separated from the $(NH_4)_2S_x$.

2. Arsenites and arseniates are distinguished (1) by H_2S, which in the cold precipitates the former instantly, and the latter only very slowly; (2) by $AgNO_3$, which in perfectly

neutral solution gives a yellow precipitate with the former, and a brown one with the latter; (3) by magnesia mixture, which precipitates only arsenic acid.

3. Stannous and stannic salts are distinguished (1) by $HgCl_2$, which gives a precipitate of HgCl or Hg with the former, and none with the latter; (2) by H_2S, which gives a brownish-black precipitate with the former, and a yellow one with the latter.

4. *Detection of Arsenic in Wall Papers, Fabrics, etc.* — Cut the material into small pieces and treat it as described in note 6, *b*, on page 74.

OXIDATION AND REDUCTION.

As many of the metals of the aluminum and iron groups exist in two or more different states of oxidation, a few general remarks on oxidation and reduction may be made with advantage at this point.

A substance is said to be oxidized when oxygen or some other acid element or radical is added to it, or when hydrogen or some other basic element or radical is taken from it.

A substance is said to be reduced when the reverse takes place.

The oxidation of one substance involves the simultaneous reduction of some other substance.

In the following examples the substance oxidized is placed first:

$$4FeO_2H_2 + O_2 + 2H_2O = 4FeO_3H_3.$$
$$3PbS + 8HNO_3 = 3PbSO_4 + 8NO + 4H_2O.$$
$$H_3AsO_3 + Cl_2 + H_2O = H_3AsO_4 + 2HCl.$$
$$SnCl_2 + 2HgCl_2 = SnCl_4 + 2HgCl.$$
$$2K_4Fe(CN)_6 + Cl_2 = 2K_3Fe(CN)_6 + 2KCl.$$

In the application of the definition of oxidation it is important to distinguish between the addition of an element and the substitution of one element or radical for another. For example, PbO dissolves in HNO_3, forming $Pb(NO_3)_2$ and H_2O. This is not an oxidation, but a simple metathesis; for the two NO_3 groups are not added, but simply take the place of their equivalent, one oxygen atom. But in the reaction: $3Pb + 8HNO_3 = 3Pb(NO_3)_2 + 2NO + 4H_2O$, the lead is oxidized, the NO_3 groups being added to it, and the HNO_3 is reduced to NO. The following additional reactions are given to illustrate further this distinction. The first reaction of each pair is an oxidation and reduction; the second, a metathetical change:

$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$
$MnO + 2HCl = MnCl_2 + H_2O.$
$SbCl_3 + 3H = Sb + 3HCl.$
$SbCl_3 + H_2O = SbOCl + 2HCl.$
$2K_2CrO_4 + 16HCl = 2CrCl_3 + 3Cl_2 + 4KCl + 8H_2O.$
$2K_2CrO_4 + 2HCl = K_2Cr_2O_7 + 2KCl + H_2O.$

In order to write reactions involving oxidation and reduction, consider first the oxides corresponding to each of the substances taking part in the reaction and known to be produced by it. It will then be evident, on the one hand, how many oxygen atoms the oxidizing agent furnishes, and on the other, how many are required for the substance oxidized, thus showing the relative number of molecules of each entering into the reaction. The method is illustrated by the following examples:

Oxidation of $FeSO_4$ with HNO_3.—The $FeSO_4$ is known to be oxidized to $Fe_2(SO_4)_3$ and the HNO_3 to be reduced to NO. Write the symbols of these compounds dualistically, regarding them as composed of the anhydride of the acid united with water or the oxide of the metal. $FeSO_4 = FeO, SO_3$; $Fe_2(SO_4)_3 = Fe_2O_3, 3SO_3$; and $2HNO_3 = H_2O, N_2O_5$. Then $2FeO + O = Fe_2O_3$ and $N_2O_5 = 2NO + O_3$. That is, $2HNO_3$ furnish 3 atoms of oxygen, and 1 atom of oxygen oxidizes 2 atoms of iron from the ferrous to the ferric condition. Hence $2HNO_3$ oxidize $6FeSO_4$. If the ferric compound thus formed is to remain in solution, free acid of some kind must be added. Its amount is readily seen by inspection.

The reactions are the following:

$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$

$6FeSO_4 + 2HNO_3 + 6HNO_3 = 2Fe_2(SO_4)_3 + 2Fe(NO_3)_3 + 2NO + 4H_2O.$

Reduction of $K_2Cr_2O_7$ with $SnCl_2$. — $SnCl_2$ corresponds to SnO; $SnCl_4$ to SnO_2; $SnO_2 = SnO + O$. $K_2Cr_2O_7 = K_2O, 2CrO_3$; $CrCl_3$ corresponds to Cr_2O_3; $2CrO_3 = Cr_2O_3 + O_3$.

Therefore $3SnCl_2$ reduce $1K_2Cr_2O_7$, and the reaction is:

$K_2Cr_2O_7 + 3SnCl_2 + 14HCl = 2CrCl_3 + 2KCl + 3SnCl_4 + 7H_2O$.

Oxidation of MnO_2H_2 by $KClO_3$ in presence of Na_2CO_3. — $KClO_3 = KCl + O_3$. $MnO_2H_2 = MnO, H_2O$. $Na_2MnO_4 = Na_2O, MnO_3$. $MnO_3 = MnO + O_2$.

Hence: $2KClO_3 + 3MnO_2H_2 + 3Na_2CO_3 = 2KCl + 3Na_2MnO_4 + 3CO_2 + 3H_2O$.

The most important oxidizing agents from an analytical point of view are: Cl, Br, and I solutions, HNO_3, $KClO_3$, $K_2Cr_2O_7$, and $KMnO_4$.

The most important reducing agents in solution are nascent hydrogen, H_2S, H_2SO_3, $SnCl_2$ and oxalic acid ($H_2C_2O_4$); at a high temperature, C, KCN, starch and other organic bodies.

It is well to remember what the usual reduction products of the important oxidizing agents are: Cl and Br are reduced to HCl and HBr; HNO_3 is reduced to NO; $KClO_3$ to KCl, $K_2Cr_2O_7$ and $KMnO_4$ in acid solution to chromic and manganous salts respectively. It should be added, however, that the reduction product of an oxidizing agent is not under all circumstances the same. For example, HNO_3 is reduced by certain metals to N_2O and NH_3; $KMnO_4$ in neutral solution is reduced only to MnO_2, not to MnO.

ALUMINUM AND IRON GROUPS.

Preliminary Tests.

Procedure. — Boil one quarter of the filtrate from the H_2S precipitate until the excess of H_2S is expelled. Add a little HNO_3 and boil again to oxidize the iron. Divide this solution into two unequal portions. Add to the larger portion 10 cc. of NH_4Cl, and NH_4OH to slight but distinct alkaline reaction; heat to boiling, and allow to stand some minutes if no precipitate separates at once. Note whether a precipitate forms and what its color is. Then add, without filtering, colorless $(NH_4)_2S$ in small quantity. If NH_4OH produces a precipitate, test the rest of the solution which has been boiled with HNO_3 for H_3PO_4 by adding an equal bulk of $(NH_4)_2MoO_4$ solution, stirring, and allowing it to stand some minutes.

Notes. — 1. If NH_4OH produces no precipitate, it proves the absence of iron, chromium, and aluminum, and the special tests for these elements may then be omitted in the subsequent analysis.

2. This conclusion is reliable, however, only when the directions are exactly followed; for AlO_3H_3 dissolves slightly in excess of NH_4OH, CrO_3H_3 dissolves in the cold (giving a pink solution) but is precipitated on boiling, and a small precipitate of any of the three is easily overlooked, owing to its transparency, unless time is allowed for the precipitate to gather in flocks.

3. Moreover, non-volatile organic matter, such as sugar, tartaric acid, etc., must not be present, for it prevents entirely the precipitation of these three elements by NH_4OH.

4. Phosphates of alkaline-earth metals, if present, are also precipitated by NH_4OH. The advantage in testing for H_3PO_4 at this point will be made clear later, and the cases in which it is useless to try the test will be discussed.

5. The color of the NH_4OH precipitate indicates which of the metals are present. AlO_3H_3 is white and transparent; CrO_3H_3, greenish blue; and FeO_3H_3, reddish brown.

6. The color of the sulphides is also important: FeS, NiS, and CoS are black; ZnS is white; and MnS is flesh-colored, but turns brown on standing in the air. If the $(NH_4)_2S$ precipitate is pure white, the subsequent tests for iron, nickel, and cobalt may be omitted.

7. The H_2S must be completely expelled at the beginning; otherwise, $(NH_4)_2S$ is formed, and the NH_4OH test is of no value.

8. In whatever condition the iron was originally present, it is in the form of a ferrous salt after the treatment with H_2S: — $2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S$. The solution is

boiled with HNO_3, since ferrous iron is not precipitated by NH_4OH in the presence of ammonium salts.

9. A black precipitate with NH_4OH shows incomplete expulsion of the H_2S, or incomplete oxidation of the iron.

10. NH_4Cl is added to prevent the precipitation of MgO_2H_2 and MnO_2H_2, which otherwise are precipitated by NH_4OH. Aside from this it is useful, for it greatly promotes the separation of AlO_3H_3, and of all the sulphides.

11. If manganese is present the solution rapidly becomes brown after the addition of NH_4OH, owing to the absorption of oxygen and precipitation of MnO_3H_3.

12. $(NH_4)_2S$ changes FeO_3H_3 to FeS, but has no effect on AlO_3H_3 and CrO_3H_3. Al_2S_3, Cr_2S_3, and Fe_2S_3 are not formed in the wet way.

13. Even if present originally as chromate, the chromium will be precipitated by NH_4OH, owing to reduction of the chromate by H_2S.

Precipitation of the Aluminum and Iron Groups.

Procedure.—If the preliminary tests show the presence of metals of the aluminum or iron groups, place the rest of the filtrate from the H_2S precipitate in a flask, add 15 or 20 cc. of NH_4Cl, NH_4OH till barely alkaline, and $(NH_4)_2S$ until the liquid after shaking causes blackening of a piece of $Pb(C_2H_3O_2)_2$ paper held above it. Heat to boiling, and shake until the precipitate will subside readily. Filter, and wash immediately with water containing a very little $(NH_4)_2S$.

Notes.—1. The notes given under the preliminary tests on the preceding page apply here also.

2. Colorless $(NH_4)_2S$ is used instead of yellow $(NH_4)_2S_x$, as the excess of sulphur is troublesome in the subsequent examination of the filtrate. For the same reason care should be taken to avoid using an excess of $(NH_4)_2S$.

3. The filtrate from the $(NH_4)_2S$ precipitate should be colorless or light yellow. A brown or black color indicates the presence of nickel, whose sulphide dissolves somewhat in excess of $(NH_4)_2S$, from which it should be precipitated by acidifying with acetic acid, boiling, and filtering through a

new filter. A pink color indicates chromium dissolved in excess of NH_4OH, from which solution it is thrown out on boiling. A green color is due to traces of finely divided FeS in suspension, which separate on standing.

4. All five sulphides oxidize rapidly in the air to sulphates; hence the addition of $(NH_4)_2S$ to the wash water.

5. NH_4OH slowly absorbs CO_2 from the air; hence if the solution is allowed to stand for some time before filtering, $BaCO_3$, $SrCO_3$, and $CaCO_3$ may precipitate.

Separation of Nickel and Cobalt.

Outline of the process.

<table>
<tr><td colspan="4">Precipitate: AlO_3H_3, CrO_3H_3, CoS, NiS, FeS, MnS, ZnS, [$Ba_3(PO_4)_2$, $Sr_3(PO_4)_2$, $Ca_3(PO_4)_2$, $MgNH_4PO_4$]. <i>Treat with dilute HCl.</i></td></tr>
<tr><td colspan="3">Residue: CoS, NiS, (FeS in small amount). <i>Dissolve in aqua regia and add NH_4OH.</i></td><td rowspan="4">Solution.</td></tr>
<tr><td rowspan="3">Precipitate:
FeO_3H_3.</td><td colspan="2">Filtrate: <i>expel NH_4 salts, add KNO_2 and $HC_2H_3O_2$.</i></td></tr>
<tr><td rowspan="2">Precipitate:
$Co(NO_2)_3 . 3KNO_2$.</td><td>Solution: <i>add NaOH.</i></td></tr>
<tr><td>Precipitate: NiO_2H_2.
<i>Test in borax bead.</i></td></tr>
</table>

Procedure.—Treat the $(NH_4)_2S$ precipitate in a dish with cold dilute HCl, made by diluting one part of acid (1.12 spec. grav.) with five of water; stir, filter when dissolved or after standing a few minutes, and if a black residue remains, wash it thoroughly. Separate it from the filter, or, if small in amount, incinerate the filter in a porcelain crucible, and dissolve the residue in a little aqua regia. Dilute, add NH_4OH in moderate excess, and filter. Add to a small portion of the filtrate a drop or two of $(NH_4)_2S$. If a black precipitate is produced, evaporate the remainder to dryness, ignite till the ammonium salts are expelled, and test a little of the residue in a borax bead in the flame of the blowpipe. Dissolve the residue in a little aqua regia, evaporate to two or three drops, add 50 cc. of KNO_2 solution and $HC_2H_3O_2$ to strongly acid reaction. Allow the mixture to stand some hours in a warm place, filter, add NaOH to the filtrate till alkaline, and if a precipitate forms, filter, and test the precipitate in a borax bead in the oxidizing flame.

Notes. — 1. The acid used is cold and dilute to avoid dissolving NiS and CoS; but even then quite appreciable quantities of these sulphides sometimes dissolve, and Ni and Co are met with later in the course of the analysis.

2. A small black residue after the HCl treatment is not necessarily NiS or CoS, but it may be FeS inclosed in sulphur.

3. Moreover, metals of the copper group, if incompletely precipitated by H_2S, appear at this point as sulphides, and may be mistaken at first for Co or Ni.

4. Action of aqua regia: $3HCl + HNO_3 = Cl_2 + NOCl + 2H_2O$. But the whole of the chlorine is available if a substance on which it can act is present: $3NiS + 6HCl + 2HNO_3 = 3NiCl_2 + 2NO + 4H_2O + 3S$.

5. NH_4OH is added to precipitate the iron, which, mechanically inclosed, may have escaped the action of the dilute HCl. The addition of $(NH_4)_2S$ then shows whether the residue consisted entirely of FeS, or whether NiS and CoS were also present.

6. The borax bead test generally proves the presence of one or other of the two metals. It is especially delicate as a test for cobalt; but in the presence of much nickel the blue color characteristic of cobalt may be obscured, and a negative result must therefore not be taken as evidence of the absence of that metal. If cobalt is absent, the color of the bead produced in the oxidizing flame — violet while hot, reddish brown when cold — proves the presence of nickel.

7. When either metal is found to be present, the tests for the other must be made with great care; for the two metals occur very commonly together.

8. The excess of NH_4OH in which the NiO_2H_2 and CoO_2H_2 are dissolved and the NH_4Cl must be completely expelled; for nickel is not completely precipitated by NaOH in their presence.

9. The yellow precipitate obtained is tri-potassium cobalt*ic* nitrite: $3KNO_2.Co(NO_2)_3$. It is decomposed by HCl and alkalies; it is decidedly soluble in water, but almost insoluble in strong KNO_2 solution. Hence the need of expelling the acid by evaporation, of having the solution concentrated, and of adding a large excess of KNO_2. The solution must be strongly acid with $HC_2H_3O_2$ to set free the HNO_2 required for oxidizing the cobalt.

Effect of the Presence of Chromium and of Alkaline-earth phosphates on the Method of Separation.

General Remarks. — Under certain circumstances to be now described, the precipitate produced by NH_4OH and $(NH_4)_2S$ may contain metals of the alkaline-earth group as well as of the aluminum and iron groups. In that case a more complicated process providing for the detection of all these metals has to be used.

Ba, Sr, Ca, and Mg are not ordinarily precipitated by NH_4OH and $(NH_4)_2S$; for their hydrates and sulphides are soluble in water (except MgO_2H_2 which dissolves in ammonium salts). But if there is present in the solution an acid radical which, combined with these metals, forms salts insoluble in water and NH_4OH, it is evident that such salts must be held in solution by an acid, and that they will be precipitated when the acid is neutralized. Consider two examples: $CaCO_3$ and $Ca_3(PO_4)_2$. Both these salts are insoluble in water, but dissolve in HCl, forming $CaCl_2$; the CO_2, being volatile, escapes, while the H_3PO_4 remains in solution. When, now, NH_4OH is added, no precipitate forms in the former case, but $Ca_3(PO_4)_2$ precipitates in the latter.

It is evident, then, that it is unnecessary to try the preliminary test for phosphates described above when the substance dissolves in water with a neutral reaction, or in any case in which no precipitate is produced by NH_4OH before the addition of $(NH_4)_2S$; for under these circumstances the

$(NH_4)_2S$ precipitate can contain no alkaline-earth phosphates; nor is it necessary in cases where the substance is unattacked by acids and has been fused with Na_2CO_3.

Alkaline-earth metals are not necessarily completely precipitated by NH_4OH even when H_3PO_4 is proved to be present, for the amount of the latter may not be sufficient to combine with the whole of the metal. Moreover, if trivalent metals are simultaneously present, the H_3PO_4 combines with them by preference, and the alkaline-earth metal may be found wholly or in part in the filtrate, there being no excess of H_3PO_4 to combine with it, or an insufficient one. When phosphates are present, it is therefore necessary to look for alkaline-earth metals both in the $(NH_4)_2S$ and in the $(NH_4)_2CO_3$ precipitates.

Besides phosphates, the precipitate produced by NH_4OH and $(NH_4)_2S$ may contain CaC_2O_4, SrC_2O_4, BaC_2O_4, or CaF_2. These are, however, met with so rarely in actual analyses, that preliminary tests for oxalic and hydrofluoric acids are dispensed with. But in case these acids are found in the subsequent examination for acids, the $(NH_4)_2S$ precipitate must be again analyzed by the process used when H_3PO_4 is present, in order to detect the alkaline-earth metals possibly in combination with them. Borates of alkaline-earth metals may also precipitate with NH_4OH, but never completely, owing to their solubility in water and ammonium salts.

It is therefore desirable to have two distinct processes of separation of the aluminum and iron groups: a short one applicable in the great majority of cases, and a longer one to be used when phosphates of alkaline-earth metals may be present, determined by the above considerations and by the preliminary test for H_3PO_4.

For an entirely different reason the short process described below cannot be used when chromium is present. This process depends on the separation of the metals with NaOH, Fe and Mn being precipitated, and Al and Zn remaining in solution. If, however, Cr is also present, Cr and Zn are precipitated with the Fe and Mn, owing to the formation of an insoluble double compound of the oxides of the first two metals.

The presence of Cr is shown by the green or purple color of the HCl solution of the $(NH_4)_2S$ precipitate. Only when this solution is colorless should it be analyzed by the NaOH process. It is hardly necessary to add that, when the $BaCO_3$ process is used only on account of the presence of Cr, all those parts of it serving for the detection or removal of alkaline-earth metals may be omitted.

Separation in the Absence of Chromium and of Phosphates.

Outline of the process.

Solution: $FeCl_2$, $MnCl_2$, $ZnCl_2$, $AlCl_3$.

Boil with HNO_3, and add NaOH in excess.

Precipitate: FeO_3H_3, MnO_2H_2.		Filtrate: *divide into two parts.*	
Dissolve a part in HCl and add $K_4Fe(CN)_6$.	*Fuse the rest with Na_2CO_3.*	*To one part add H_2S.*	*To the other add HCl and NH_4OH.*
Precipitate: $Fe_4(Fe(CN)_6)_3$	Na_2MnO_4 formed.	Precipitate: ZnS.	Precipitate: AlO_3H_3.

Procedure. — If the previous tests have shown the absence of phosphates of alkaline-earth metals, and the filtrate from the NiS and CoS is colorless, boil it till the H_2S is completely expelled; add HNO_3 and boil again; evaporate nearly to dryness, dilute with a little water, add NaOH till the liquid turns red litmus paper blue, and then add 5 to 10 cc. more. Filter off and wash the precipitate.

Notes. — 1. If the H_2S is not completely expelled, S is precipitated on boiling with HNO_3, and ZnS may be precipitated on the addition of NaOH.

2. The evaporation expels the free acid, which would require NaOH for its neutralization; and the use of an unnecessary amount of this reagent is to be avoided, as it often contains small quantities of Al or silicic acid as impurity.

3. The small quantities of NiS and CoS dissolved by the dilute HCl are precipitated in the form of hydrates by NaOH. A precipitate produced by this reagent may, therefore, consist entirely of these metals. Their presence does not interfere with the tests for Fe and Mn.

4. In the presence of much Fe, the $BaCO_3$ process must be used to detect small quantities of Zn; for the NaOH precipitate may then contain even one per cent. of Zn.

5. If a solution containing Cr were analyzed by this process, the Cr would be found in the filtrate from the NaOH precipitate, unless Zn were also present, in which case both metals would be precipitated. CrO_3H_3, unlike AlO_3H_3, is precipitated from its NaOH solution by boiling.

Procedure. — Test a portion of the NaOH precipitate for Fe by dissolving in dilute HCl, diluting with water, and adding three or four drops of $K_4Fe(CN)_6$ solution. Also test a part of the solution with KSCN. (If Fe is present, test a freshly prepared solution of the original substance in H_2O or HCl with $K_3Fe(CN)_6$ and KCNS). Examine another portion for Mn by fusing on platinum foil with six parts of Na_2CO_3, heating sufficiently to fuse the mixture to a thin liquid.

Notes. — 1. Strong HCl decomposes $K_4Fe(CN)_6$, so that the test for iron may be obtained from the reagent alone, if the acid is not diluted. Even weak acids decompose $K_4Fe(CN)_6$ on standing.

2. $Fe_4(Fe(CN)_6)_3$ dissolves somewhat in an excess of $K_4Fe(CN)_6$; hence the addition of only a few drops of the latter. Most of the other metals give precipitates with $K_4Fe(CN)_6$; it is the blue color of the precipitate which proves the presence of iron.

3. By the fusion Na_2MnO_4 is formed, the oxygen required being taken from the air. Its formation is indicated by a green color of the fused mass. The test is exceedingly delicate. It is well to make sure that the platinum foil used is perfectly clean by fusing Na_2CO_3 on it before trying the test. The iron remains unchanged as Fe_2O_3.

Procedure. — Test a part of the filtrate for zinc by passing in a *little* H_2S. Acidify the remainder with HCl, make slightly alkaline with NH_4OH; heat the solution gently, and allow it to stand half an hour if no precipitate is visible at first.

Notes.—1. If much H_2S is passed in, the NaOH is changed to NaSH, and AlO_3H_3 precipitates, and may be mistaken for ZnS.

2. A dark colored precipitate is sometimes obtained in testing for zinc with H_2S. This often arises from the presence of iron, and sometimes from that of lead which was not completely precipitated by H_2S originally, but was thrown out by $(NH_4)_2S$ and dissolved by the dilute HCl. To detect zinc in such a case, the dark precipitate should be filtered off and dissolved on the filter in a little hot dilute HCl; a few drops of HNO_3 should then be added, the solution boiled, NH_4OH added in excess, the precipitate filtered out, and the filtrate tested for zinc with H_2S.

3. ZnO_2H_2 precipitates, if the solution is made just neutral with NH_4OH. A slight excess is necessary to redissolve it. A large excess dissolves AlO_3H_3.

4. When the precipitate of AlO_3H_3 obtained is small, it is advisable to make a blank experiment with the same quantity of NaOH under exactly the same conditions, in order to make sure that the precipitate does not come from impurity in that reagent, or from the vessels used.

5. Precipitates of silicic acid are sometimes obtained in the test for Al. For a method of removing this acid at the beginning of the analysis, see page 69. In order to distinguish between AlO_3H_3 and H_2SiO_3, fuse the precipitate on platinum foil with $KHSO_4$, dissolve the fused mass in hot water, filter, and make slightly alkaline with NH_4OH. By the fusion the silicic acid is dehydrated and made insoluble; Al passes into solution in the form of $Al_2(SO_4)_3$.

Separation in the Presence of Chromium or of Phosphates.

Outline of the process.

(See the following page.)

Remark. — The directions for that part of the following process which serves for the removal and detection of phosphoric acid and the alkaline-earth metals are inclosed in brackets, and may be omitted when these substances are known to be absent. The notes referring to it are designated with an asterisk.

Outline of the process.

<table>
<tr><td colspan="10">Solution: $AlCl_3$, $CrCl_3$, $FeCl_2$, $MnCl_2$, $ZnCl_2$, $BaCl_2$, $SrCl_2$, $CaCl_2$, $MgCl_2$, H_3PO_4.</td></tr>
<tr><td colspan="2">Add H_2SO_4 and alcohol to a part.</td><td>Boil a part with HNO_3 and add $K_4Fe(CN)_6$.</td><td colspan="7">Boil the rest with HNO_3, add $FeCl_3$ and $BaCO_3$.</td></tr>
<tr><td rowspan="2">Precipitate:
$BaSO_4$,
$SrSO_4$,
$CaSO_4$.
Fuse with Na_2CO_3; add water.</td><td rowspan="4">Filtrate. Reject.</td><td rowspan="4">Precipitate: Ferric ferrocyanide.</td><td colspan="3">Precipitate: FeO_3H_3, AlO_3H_3, CrO_3H_3, $FePO_4$, ($BaCO_3$). Dissolve in HCl and add H_2SO_4.</td><td colspan="4">Filtrate. Add NH_4OH and $(NH_4)_2S$.</td></tr>
<tr><td rowspan="3">Precipitate: $BaSO_4$.</td><td colspan="2">Filtrate. Add NaOH and boil.</td><td colspan="2">Precipitate: MnS, ZnS. Dissolve in HCl and add NaOH.</td><td colspan="2">Filtrate. Add $(NH_4)_2CO_3$ and $(NH_4)_2C_2O_4$.</td></tr>
<tr><td>Residue:
$BaCO_3$,
$SrCO_3$,
$CaCO_3$.
Add HNO_3.</td><td>Precipitate:
FeO_3H_3,
CrO_3H_3.
Fuse with Na_2CO_3 and $KClO_3$.</td><td>Filtrate: add HCl and NH_4OH.</td><td>Precipitate:
MnO_2H_2.
Fuse with Na_2CO_3.</td><td>Filtrate. Add H_2S.</td><td rowspan="2">Precipitate:
$BaCO_3$,
$SrCO_3$,
$CaCO_3$,
CaC_2O_4.
Reject.</td><td>Filtrate. Add Na_2HPO_4.</td></tr>
<tr><td>Solution:
$Ba(NO_3)_2$,
$Sr(NO_3)_2$,
$Ca(NO_3)_2$.</td><td>Na_2CrO_4 formed.</td><td>Precipitate: AlO_3H_3.</td><td>Na_2MnO_4 formed.</td><td>Precipitate: ZnS.</td><td>Precipitate: $MgNH_4PO_4$.</td></tr>
</table>

Procedure. — Boil the solution of the $(NH_4)_2S$ precipitate in HCl till the H_2S is completely expelled. [Evaporate a third of it just to dryness. To the residue add 10–20 cc. of dilute H_2SO_4 and three volumes of alcohol. Allow the mixture to stand a few minutes, filter, and wash with a mixture of three volumes of alcohol and one of water. Dry the precipitate and fuse it on platinum foil with five times its bulk of Na_2CO_3. Boil the fused mass with water till disintegrated, filter, and wash the residue thoroughly. Dissolve it in dilute HNO_3, and examine the solution for Ba, Sr, and Ca, as described on page 46.]

Notes. — 1. The precipitate obtained after the addition of $(NH_4)_2S$ may consist of FeS, MnS, ZnS, CoS, NiS, AlO_3H_3, CrO_3H_3, $AlPO_4$, $CrPO_4$, $Ba_3(PO_4)_2$, $Sr_3(PO_4)_2$, $Ca_3(PO_4)_2$ $MgNH_4PO_4$, BaC_2O_4, SrC_2O_4, CaC_2O_4, and CaF_2; also of borates of alkaline-earth metals, and silicic acid, if it has not been previously removed. All these substances except CaF_2 and H_2SiO_3 dissolve readily in dilute HCl.

2.* A portion of the solution is tested for Ba, Sr, and Ca, at this point, since $BaCO_3$ is to be added to the remainder as a reagent.

3.* H_2SO_4 precipitates Ba and Sr completely if allowed to stand a few minutes. Ca is also partly precipitated, if the solution is concentrated, but never completely until alcohol is added, owing to its slight solubility in water.

4.* Fusing with Na_2CO_3 converts the sulphates to carbonates. If the Na_2SO_4 produced is not washed out completely, the sulphates are again formed on treating with HNO_3.

5.* If $(NH_4)_2CO_3$ produces a precipitate in the filtrate from the $(NH_4)_2S$ group, the solution of that precipitate in HNO_3 should be united with the HNO_3 solution here obtained, in order to avoid two separate analyses for the alkaline earth metals.

Procedure. — Boil the rest of the HCl solution with a small quantity of HNO_3, dilute a little of it and test with $K_4Fe(CN)_6$, added drop by drop, or with KCNS. (If Fe is present, test a freshly prepared solution of the original substance in H_2O or HCl with $K_3Fe(CN)_6$ and KCNS.)

Treat the remainder as follows: [Add $FeCl_3$ little by little, till a drop of the solution tested on a watch glass gives a yellow precipitate with NH_4OH.] Evaporate the solution to a small bulk to expel most of the acid, add Na_2CO_3 as long as the precipitate which forms can be made to redissolve on shaking. Place in a small flask, dilute with water to at least 200 cc., cool if still hot, and add $BaCO_3$, avoiding a large excess. Allow the mixture to stand, with frequent shaking, for half an hour. Filter and wash the precipitate.

Notes. — 1. The solution tested with KCNS should be dilute and cold; for otherwise the HNO_3 rapidly destroys the reagent. NO_2 is thereby formed, which itself gives a red color with KCNS.

2.* If $FeCl_3$ were not added, the phosphates of the alkaline-earth metals would precipitate when the solution is made neutral with $BaCO_3$. But its addition causes precipitation of the H_3PO_4 in the form of $FePO_4$, and thus allows the bivalent metals to pass into the filtrate in the form of chlorides.

3.* The test with NH_4OH shows when sufficient $FeCl_3$ has been added to combine with all the H_3PO_4; for before that point is reached, white $FePO_4$ precipitates; but as soon as an excess is present, brown FeO_3H_3 precipitates with it.

4. $BaCO_3$ precipitates only the trivalent metals, aluminum, chromium, and ferric iron, leaving all the bivalent metals in solution.

5. Na_2CO_3, on the other hand, being soluble, precipitates all the metals. The addition of enough to produce a permanent precipitate is therefore fatal to the separation.

6. The solution must be cold; for $BaCO_3$ does precipitate from hot solutions certain bivalent metals. These are also precipitated if sulphates are present in the solution, since insoluble $BaSO_4$ is thus formed.

7. The precipitate obtained by following the above directions consists of the excess of $BaCO_3$, of $FePO_4$ of FeO_3H_3, AlO_3H_3, and CrO_3H_3. Reactions: $2FeCl_3 + 3BaCO_3 + 3H_2O = 2FeO_3H_3 + 3BaCl_2 + 3CO_2$, etc.

Procedure. — Dissolve the $BaCO_3$ precipitate in dilute HCl, heat to boiling, and add, without filtering, dilute

H_2SO_4; allow it to stand a few minutes, filter out the $BaSO_4$, add to the filtrate NaOH to strong alkaline reaction, boil two or three minutes in a porcelain dish, filter, and test the precipitate for chromium by fusing on platinum foil with Na_2CO_3 and $KClO_3$, boiling the fused mass with water, filtering, adding $HC_2H_3O_2$ to acid reaction, boiling to expel CO_2, and then adding $Pb(C_2H_3O_2)_2$. Test the filtrate from the NaOH precipitate for aluminum by acidifying it with HCl, adding NH_4OH till very slightly alkaline, heating and allowing it to stand, if no precipitate is visible at first.

Notes. — 1. Dilute HCl is used for dissolving the $BaCO_3$; for $BaCl_2$ is insoluble in strong HCl. The solution should be at the boiling temperature when H_2SO_4 is added; for the $BaSO_4$ is then less likely to pass through the filter. A slightly turbid filtrate need not, however, be again filtered.

2. By fusion with Na_2CO_3 and $KClO_3$, CrO_3H_3 is changed to Na_2CrO_4, which gives a yellow color to the fused mass.

3. If, however, Mn is present in the substance, enough of it is almost always retained in the $BaCO_3$ precipitate to give the characteristic green coloration of Na_2MnO_4 on fusing. The yellow color of the Na_2CrO_4 is then obscured, and it is necessary to dissolve the fused mass in water, to boil (with addition of a few drops of alcohol, if necessary), in order to reduce the Na_2MnO_4 to MnO_2, to filter, and add $HC_2H_3O_2$ and $Pb(C_2H_3O_2)_2$. The $HC_2H_3O_2$ neutralizes the Na_2CO_3, and the $Pb(C_2H_3O_2)_2$ precipitates $PbCrO_4$.

4. The precipitate produced by NaOH is usually very bulky, owing to the presence of a large amount of iron, and a common mistake in testing for chromium is to fuse only a small portion of this precipitate. A large part or, better, the whole precipitate should be employed. It is best dried on the filter, whereby its volume is greatly reduced, before mixing with Na_2CO_3 and $KClO_3$.

5. When Cr is present, small quantities of it sometimes precipitate in the test for Al, owing to insufficient boiling of the NaOH solution. It is distinguished by the green color of the precipitate after time has been allowed for its separation from the liquid. To test for Al in it, the precipitate should

be filtered off and dissolved in a little NaOH, the solution boiled and filtered, and the test for Al tried in the filtrate.

6. Consult notes 4 and 5 on page 38.

Procedure. — Acidify the filtrate from the $BaCO_3$ precipitate with a few drops of HCl, and boil two or three minutes to expel CO_2. [Make slightly alkaline with NH_4OH and add $(NH_4)_2S$, avoiding an excess. Filter out and wash any precipitate that may form, dissolve it in HCl, boil till the H_2S is completely expelled], add NaOH till alkaline; filter, test the precipitate for Mn by fusion with Na_2CO_3, and the filtrate for Zn by passing in H_2S. [To the filtrate from the $(NH_4)_2S$ precipitate add $(NH_4)_2CO_3$ and $(NH_4)_2C_2O_4$; filter; reject the precipitate; concentrate the filtrate as much as possible, add to it one third its volume of NH_4OH and a little Na_2HPO_4, stir, and allow it to stand over night if no precipitate appears at once.]

Notes. — 1.* If the CO_2 is not expelled, the alkaline-earth carbonates will be precipitated when NH_4OH and $(NH_4)_2S$ are added.

2. The $(NH_4)_2S$ precipitate consists of MnS and ZnS. If dark colored, it may contain small quantities of NiS and CoS, which were dissolved by the dilute HCl used at first; in that case it should be tested in a borax bead. FeS will also be precipitated here if the oxidation with HNO_3 was incomplete.

3.* $(NH_4)_2CO_3$ and $(NH_4)_2C_2O_4$ are added to remove the Ba, Sr and Ca, which would otherwise precipitate with Na_2HPO_4 in the Mg test. $(NH_4)_2C_2O_4$ is added since it precipitates Ca more completely than $(NH_4)_2CO_3$. $MgNH_4PO_4$ is somewhat soluble in H_2O; hence the solution must be concentrated, and contain a large quantity of NH_4OH, in which the precipitate is less soluble.

ADDITIONAL REACTIONS OF METALS OF THE ALUMINUM AND IRON GROUPS.

Behavior towards the Alkalies. — All metals of these groups are precipitated both by NaOH and NH_4OH. Excess of cold

NaOH dissolves AlO_3H_3, CrO_3H_3, and ZnO_2H_2; by boiling the solution, CrO_3H_3 is precipitated. Excess of NH_4OH readily dissolves NiO_2H_2, CoO_2H_2, and ZnO_2H_2; in the presence of NH_4Cl, MnO_2H_2 and FeO_2H_2 also dissolve.

Ferrous and Ferric Salts. — These are distinguished (1) by $K_3Fe(CN)_6$, which gives a blue precipitate with ferrous, and none with ferric salts; (2) by KCNS, which gives a deep red color with ferric salts, and no color with ferrous.

Chromates and Permanganates. — These are reduced by H_2S to chromic and manganous salts. Special tests for chromic acid will be given later under "Detection of the Acids."

ALKALINE-EARTH AND ALKALI GROUPS.

Outline of the process.

(See the following page.)

Procedure. — To the filtrate from the NH_4OH and $(NH_4)_2S$ precipitate add a little more NH_4OH, and then $(NH_4)_2CO_3$ in slight excess. Warm the solution gently for some minutes; if a precipitate forms, filter it out and wash it. Whether a precipitate forms or not, add to a small portion of the filtrate, or of the solution in which $(NH_4)_2CO_3$ gives no precipitate, a little $(NH_4)_2SO_4$, and to another small portion a little $(NH_4)_2C_2O_4$; if either or both of these reagents produce a precipitate, add it or them to the whole solution and filter through a new filter. Test the precipitate no further; but examine the filtrate for Mg and alkali metals as described below.

Notes. — 1. The filtrate from the $(NH_4)_2S$ precipitate should be colorless or light yellow. (See note 3, page 31.) If it has become turbid through separation of sulphur from standing in the air, or if it becomes so on warming, acidify the solution with HCl, boil for five or ten minutes, and filter; then add NH_4OH and $(NH_4)_2CO_3$. The $(NH_4)_2S$ is thus destroyed, and the boiling prevents the sulphur from passing through the filter.

Outline of the process.

<table>
<tr><td colspan="7">Solution: Ba, Sr, Ca, Mg, K, Na, and NH_4 salts. *Add* $(NH_4)_2CO_3$.</td></tr>
<tr><td colspan="3">Precipitate: $BaCO_3$, $SrCO_3$, $CaCO_3$. *Dissolve in* HNO_3 *and evaporate the solution to dryness. Treat the residue with alcohol-ether mixture.*</td><td colspan="4">Filtrate. *Add* $(NH_4)_2C_2O_4$ *and* $(NH_4)_2SO_4$.</td></tr>
<tr><td colspan="2" rowspan="2">Residue: $Ba(NO_3)_2$, $Sr(NO_3)_2$. *Dissolve in water, and add* K_2CrO_4.</td><td>Solution: *add dilute* H_2SO_4.</td><td rowspan="4">Precipitate: CaC_2O_4, $BaSO_4$.</td><td colspan="3">Filtrate. *Divide into two parts.*</td></tr>
<tr><td rowspan="3">Precipitate: $CaSO_4$.</td><td>*Add* NH_4OH *and* Na_2HPO_4.</td><td colspan="2">*Expel* NH_4 *salts, and dissolve the residue in water.*</td></tr>
<tr><td rowspan="2">Precipitate: $BaCrO_4$.</td><td>Solution: *add* $(NH_4)_2CO_3$.</td><td rowspan="2">Precipitate: $MgNH_4PO_4$.</td><td>*Test in flame.*</td><td>*Add* H_2PtCl_6.</td></tr>
<tr><td>Precipitate: $SrCO_3$.</td><td>Yellow color, Na.</td><td>Precipitate: K_2PtCl_6.</td></tr>
</table>

2. Ammonium salts considerably increase the solubility of the alkaline-earth carbonates in water, so that small quantities of the metals might escape detection if $(NH_4)_2CO_3$ were alone employed; hence the further tests with $(NH_4)_2SO_4$, and $(NH_4)_2C_2O_4$ for Ba and Ca respectively. Even if already detected in the $(NH_4)_2CO_3$ precipitate, the traces of these metals must be so removed, as otherwise they will precipitate in the test for Mg.

3. The presence of ammonium salts is necessary, however, in order to avoid the precipitation of $MgCO_3(NH_4)_2CO_3$. For the same reason the solution should be moderately dilute and not stand long before filtering.

Procedure. — Dissolve the precipitated carbonates in a small quantity of dilute HNO_3. Evaporate the solution to dryness in a small porcelain dish, and heat quite strongly on an iron plate until no odor of HNO_3 can be detected. As soon as it is cold, rub the contents of the dish to powder by means of a pestle, add 5–10 cc. of a mixture of equal volumes of absolute alcohol and ether, and triturate with the pestle for two or three minutes. Filter, and add two drops of dilute H_2SO_4 to the *filtrate.* Wash the *residue* on the filter with small quantities of the alcohol-ether mixture until the wash water shows no turbidity with a drop of dilute sulphuric acid; then dissolve it in 10–20 cc. of water, and filter if not perfectly clear. To a third of the solution add two or three drops of acetic acid, dilute it with 50 cc. of water, heat to boiling, and add gradually K_2CrO_4 until present in slight excess. *If no precipitate forms,* add NH_4OH and $(NH_4)_2CO_3$ to the remaining two thirds of the aqueous solution. *If a precipitate forms,* treat the remainder of the solution in just the same way as the first third was treated, unite the two portions, heat to boiling, and filter. Then add to the filtrate NH_4OH and $(NH_4)_2CO_3$.

Notes. — 1. In order that the separation of the nitrates by the alcohol-ether mixture may be complete, it is essential that they be completely anhydrous; for $Sr(NO_3)_2$ is very readily soluble in water, and $Ba(NO_3)_2$ moderately so. The temperature, therefore, must be sufficiently high and long continued to effect dehydration; it may reach 180° without injury, but too high a temperature would convert the nitrates to oxides. Since the nitrates are hygroscopic, they must not be left exposed to the air; but they should be treated immediately with the solvent.

2. If the precipitate produced by H_2SO_4 is very small, it may be due to a trace of $Sr(NO_3)_2$ dissolved, owing to the presence of water, by the alcohol-ether mixture. In that case, therefore, collect it upon a small filter, pour through the latter repeatedly 5 cc. of a hot, concentrated (25 per cent.) solution of $(NH_4)_2SO_4$, to which a few drops of NH_4OH have been added, make barely acid with acetic acid, and add a few drops of $(NH_4)_2C_2O_4$. The formation of a precipitate shows conclusively the presence of Ca, for the minute quantities of $SrSO_4$ soluble in $(NH_4)_2SO_4$ are not precipitated by $(NH_4)_2C_2O_4$.

3. In order that the precipitation of $BaCrO_4$ may be complete, the quantity of free $HC_2H_3O_2$ present must be small. The solution is diluted to prevent the precipitation of strontium. It is precipitated hot, since otherwise $BaCrO_4$ is liable to pass through the filter. A perfectly clear filtrate must always be obtained before adding $(NH_4)_2CO_3$.

4. In order to detect minute quantities of Ba, Sr, and Ca, it is advisable to examine the nitrates with the spectroscope before treating them with the alcohol-ether mixture.

Procedure. — Evaporate the filtrate from the $(NH_4)_2CO_3$ (or $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$) precipitate in a porcelain vessel till ammonium salts begin to crystallize out. Acidify the liquid with HCl, filter, and add to a *portion* of it a third its volume of NH_4OH and some Na_2HPO_4. Rub the sides of the tube with a glass rod, and if no precipitate appears, allow it to stand over night.

Evaporate the *remainder* of the solution to dryness in a small porcelain dish, and ignite the residue not above a faint red heat until no more white fumes come off, taking care to heat the sides as well as the bottom of the dish. Dissolve in a little water, filter, and evaporate to dryness in a small beaker; note the quantity of the residue, and introduce a little of it into a flame on a platinum wire. Dissolve in the least possible quantity of water, add a few drops of H_2PtCl_6, stir, and allow the solution to stand.

Notes. — 1. Concerning the precipitation of $MgNH_4PO_4$ see note 4, page 43. All other metals except arsenic and the alkalies are also precipitated by Na_2HPO_4; so the magnesium test can be made only after they are removed. The precipitate should be crystalline; if flocculent it may consist of $AlPO_4$, present here by reason of the solubility of AlO_3H_3 in NH_4OH and the use of too large a quantity of that reagent in precipitating the aluminum and iron groups.

2. Presence of $MgCl_2$ does not interfere with the H_2PtCl_6 test for potassium. When present in large amount, however, it is sometimes desirable to remove it, in order to form, from the amount of residue left after ignition, an approximate idea of the quantity of alkali metals present. It is removed by adding BaO_2H_2 to the solution from which the ammonium salts have been expelled, boiling, filtering out the MgO_2H_2, precipitating the barium from the filtrate with NH_4OH and $(NH_4)_2CO_3$, filtering, evaporating the filtrate, and igniting the residue to expel ammonium salts. By this same method all other metals (except arsenic) can be removed from a solution to be tested for alkalies.

3. Since ammonium salts, like those of potassium, give a precipitate with H_2PtCl_6, great care must be taken to remove them completely; ignition above faint redness, however, volatilizes KCl and NaCl.

4. No satisfactory precipitant for sodium is known. The flame test is so exceedingly delicate that only when the yellow color is intense and persistent is it to be taken as an indication of sodium in appreciable quantity. At best, however, the flame test is very unsatisfactory; it is therefore always advisable to determine approximately, as directed in the Procedure, the amount of residue left after expulsion of the ammonium salts; for, in this way, an idea can be formed of the amount of Na present, when Mg and K are absent, or when

present only in small amounts. If Mg or K are present in considerable amounts, it is even usually advisable to remove them by precipitation, and to determine the amount of Na in the filtrate by evaporation. Magnesium is best removed as described in note 2 above. To remove potassium, add H_2PtCl_6 in the usual manner; evaporate the filtrate to dryness, ignite the residue at a temperature below redness and treat it with water, filter the solution and finally evaporate it to dryness. By the ignition the Na_2PtCl_6 and H_2PtCl_6 are destroyed, Pt and NaCl alone remaining in the dish.

5. K_2PtCl_6 is soluble in 100 parts of cold and 20 parts of hot water; hence the need of having the solution cold and very concentrated, and of allowing it to stand.

6. Very small quantities of K and Na, like those Ba, Sr, and Ca, are best detected with the aid of the spectroscope. This method does not answer the ordinary purposes of analysis, however; for it gives but little idea of the quantity of the element present, and does not distinguish unimportant traces from considerable amounts.

Procedure. — Test a portion of the original solid substance for ammonium salts by mixing it in a small beaker with solid CaO_2H_2 moistened with a little water. Cover the beaker with a watch glass with a piece of moist red litmus paper adhering to the under side, and heat gently.

DETECTION OF THE ACIDS.

GENERAL REMARKS.

The number of acids to be tested for is often restricted by the solubility of the substance taken in connection with the metals already found in it. A substance completely soluble in water containing a certain metal cannot contain any acid known to form an insoluble salt with that metal; for example, a barium salt soluble in water need not be tested for sulphate, chromate, phosphate, oxalate, borate, carbonate, or fluoride; a barium salt soluble in dilute acids cannot contain sulphate. But, on the other hand, when the substance is insoluble, it is not safe to conclude that all acids forming soluble salts with the metals present are therefore absent; for the solution of such salts may be prevented by the presence of insoluble substances which hold them back mechanically or by reason of chemical combination; for example, $Ba(NO_3)_2$ is retained in this way by $BaSO_4$. Moreover, many salts which when normal are readily soluble are insoluble when basic; for example, basic lead nitrate, $Pb(OH)NO_3$.

In order to determine what acids are excluded by the solubility of the substance, the solubility of the various salts of the metals present must be considered. The following brief statement will be of assistance:

1. All K, Na, and (NH_4) salts are soluble in water (except K_2PtCl_6, $(NH_4)_2PtCl_6$, $KHC_4H_4O_6$, and $(NH_4)HC_4H_4O_6$).

2. All nitrates, chlorates, and acetates are soluble in water (except certain basic nitrates and acetates).

3. All carbonates, phosphates, borates, oxalates, arseniates, and arsenites, except those of the alkalies, are insoluble or only slightly soluble in water, but are readily soluble in dilute acids.

4. All chlorides, bromides, and iodides, except the lead, silver, and mercurous compounds and HgI_2, and all sulphates, except those of Ba, Sr, Ca, and Pb, are soluble in water.

The number of acids to be tested for is further limited in many cases by the nature of the substance analyzed. For example, it is useless to test a mineral for organic and cyanogen acids, or, in general if insoluble in water, for nitrates, chlorates, bromides, and iodides; alloys contain no acids; etc.

DIVISION OF THE ACIDS INTO GROUPS.

The detection of the acids does not require, like that of the metals, their separation from one another. They are, nevertheless, divided into groups according to their behavior toward certain general reagents, which, however, serve to show the presence or absence of a whole group of acids, and not to separate one group from another.

The acids are primarily divided into two classes:

1. Those whose salts blacken and emit a burnt odor when ignited in a closed tube; that is, the organic acids.
2. Those whose salts do not behave thus; that is, the inorganic acids.

Notes. — 1. Blackening does not necessarily prove an organic *acid.* Starch, sugar, and other organic substances also char.

2. Blackening, unaccompanied by a burnt odor, is not due to organic matter. Cu, Co, and Ni salts may cause it, owing to expulsion of the acid and change to the black oxides.

3. The presence of organic matter is generally best detected by heating the substance *suddenly* to a high temperature.

4. Oxalic acid, an organic acid, is here classed with the inorganic; for its salts do not char, or char but slightly.

Organic Acids. — These are exceedingly numerous, and no attempt to group them separately will be made. Acetic and tartaric acids, the two most commonly met with, are the only ones that will be considered in this course.

Inorganic Acids. — These including the two organic acids, acetic and tartaric, are divided into groups as follows:

GROUP I. *Sulphuric Acid Group.* — Acids precipitated from neutral solution by $BaCl_2$. They are: H_2SO_4, H_2CrO_4, H_3PO_4, H_3BO_3, $H_2C_2O_4$, HF, H_2CO_3, H_4SiO_4, $H_2C_4H_4O_6$. (H_2SO_3, $H_2S_2O_3$, H_3AsO_3, H_3AsO_4.)

Group II. *Halogen Group.* — Acids precipitated from dilute HNO_3 solution by $AgNO_3$ They are: HCl, HBr, HI, HCN, H_2S, $H_3Fe(CN)_6$, $H_4Fe(CN)_6$.

Group III. *Nitric Acid Group.* — Acids not precipitated by $BaCl_2$ nor by $AgNO_3$. They are: HNO_3, $HClO_3$, $HC_2H_3O_2$.

Note. — Though $AgNO_3$ precipitates none of the acids of the first group from an acid solution, it precipitates all of them except H_2SO_4 and HF from a neutral solution. The acids of the second group are also precipitated by $AgNO_3$ in neutral solution. From an acid solution $BaCl_2$ precipitates only H_2SO_4.

General Tests.

Procedure. — If the solution is acid, make a portion of it slightly alkaline with NH_4OH; if it is alkaline with Na_2CO_3, acidify a portion with HNO_3, boil it a few minutes to expel CO_2, and make it alkaline with NH_4OH; add $BaCl_2$ and $CaCl_2$, and if no precipitate forms at once, allow the solution to stand some minutes. If a precipitate forms, add HCl in considerable quantity.

Notes. — 1. Non-formation of a precipitate in neutral solution proves the absence of all acids of the first group except H_3BO_3, which is precipitated by $BaCl_2$ and $CaCl_2$ only from rather concentrated solutions.

2. This conclusion is correct, however, only when no considerable quantity of ammonium salt is present; for, with the exception of $BaSO_4$ and CaC_2O_4 all these precipitates dissolve in ammonium salts somewhat, and some of them (the borate, fluoride, and tartrate) dissolve quite readily.

3. If the precipitate dissolves completely in HCl, H_2SO_4 is absent; if it is not completely soluble, H_2SO_4 is present, and other acids of its group may also be present. Owing to the solubility of their Ba and Ca salts in ammonium salts, their presence or absence cannot be determined by filtering and neutralizing the filtrate from the $BaSO_4$ with NH_4OH.

4. The precipitates are all white except the chromate.

5. $CaCl_2$ is added, since CaC_2O_4, CaF_2, and $CaC_4H_4O_6$, are more insoluble than the corresponding barium salts.

Procedure. — Acidify a portion of the solution with HNO_3, and add $AgNO_3$. If a precipitate forms, filter it off and test the filtrate with more $AgNO_3$ to insure complete precipitation. Then carefully pour a little dilute ammonia down the sides of the tube so as to form a layer on top. Note whether a precipitate forms at the junction, and what its color is.

Notes. — 1. Non-formation of a precipitate in acid solution proves the absence of the halogen group. If no precipitate is obtained in neutral solution, all acids of the sulphuric acid group except H_2SO_4 and HF are absent.

2. The color of the silver precipitates taken in connection with their solubility in HNO_3 is an important indication. AgI, Ag_3PO_4, and Ag_3AsO_3 are yellow; AgBr is yellowish white; Ag_3AsO_4 and $Ag_3Fe(CN)_6$ are brownish red; Ag_2CrO_4 is dark red; Ag_2S is black, and the remainder are white. Ag_2CO_3, white at first, rapidly turns yellow, and on boiling, brown owing to change to Ag_2O.

3. All the precipitates with the exception of AgI, Ag_2S and $Ag_4Fe(CN)_6$ dissolve in NH_4OH, most of them very readily; AgBr dissolves only sparingly. Therefore $AgNO_3$ precipitates chromates, phosphates, etc., only from a perfectly neutral solution. As the whole solution is not easily made exactly neutral, the NH_4OH is added on top, by which a neutral layer is formed at the junction.

4. $Ag_2C_2O_4$ dissolves in HNO_3 with some difficulty; hence, if considerable HNO_3 is not added, it might be mistaken for a halogen compound.

5. A grayish brown precipitate of Ag_2O, very soluble in HNO_3, NH_4OH, and NH_4NO_3, may form, even when no acids of the first and second groups are present.

Procedure. — Add a few drops of strong H_2SO_4 to some of the finely powdered substance placed in a very small test-tube, and heat gently — not enough to cause volatilization of the H_2SO_4.

Notes. — 1. Salts of the various acids give indications as follows:

Chromates, sulphates, phosphates, and borates remain unchanged.

Silicates remain unchanged, or decompose with separation of silicic acid.

Sulphites evolve SO_2, recognized by its odor.

Thiosulphates evolve SO_2 and give a precipitate of sulphur.

Oxalates and carbonates effervesce, owing to escape of CO_2 (accompanied by CO in the case of oxalates).

Fluorides evolve HF, which etches the watch glass on which the test is tried.

Chlorides evolve HCl, recognized by its odor.

Bromides and iodides evolve Br and I, recognized by their color and odor.

Cyanides evolve HCN, recognized by its odor.

Sulphides evolve H_2S, known by its odor and reaction with $Pb(C_2H_3O_2)_2$.

Nitrates evolve HNO_3, recognized by its odor.

Chlorates evolve ClO_2, a green gas which smells like chlorine and colors the H_2SO_4 intensely yellow.

Acetates evolve $HC_2H_3O_2$, known by its odor.

Tartrates char and cause blackening of the H_2SO_4.

2. These indications should not be taken as conclusive, but should be confirmed by appropriate special tests. This is especially true where the results are negative, owing to the fact that certain insoluble salts are not decomposed as above stated.

SPECIAL TESTS.

By the considerations stated on pages 50 and 51, and by the $BaCl_2$ and $AgNO_3$ tests, the examination for acids is much simplified. Moreover, in the analysis for metals, the presence of many acids, namely: H_2CO_3, H_2S, HCN, H_2SO_3, $H_2S_2O_3$, $HClO_3$, on addition of HCl; H_3AsO_3, H_3AsO_4, H_2CrO_4, by the action of H_2S; — will generally have been demonstrated. For the acids not already detected, or not proved absent, special tests must be tried, as described below.

SULPHURIC ACID GROUP.

Chromic Acid.

1. Reducing agents, such as nascent hydrogen, strong HCl, H_2S in presence of acid, reduce chromates to chromium salts, the color of the solution changing from yellow or red to green. In the presence of insufficient acid H_2S effects only partial reduction, producing a brown precipitate of hydrated CrO_2, which, in the analysis for metals, might be mistaken for a sulphide of the H_2S group.

2. $Pb(C_2H_3O_2)_2$ precipitates $PbCrO_4$, insoluble in $HC_2H_3O_2$.

3. Acids change the yellow color of solutions of normal chromates to red, owing to formation of dichromates.

Sulphuric Acid.

The $BaCl_2$ test in presence of HCl is conclusive for this acid. It is simply necessary to avoid the addition of much HCl; for this prevents the precipitation of small quantities of $BaSO_4$, and may cause the precipitation of $BaCl_2$.

Sulphurous and Thiosulphuric Acids.

These are detected by the action of H_2SO_4 on the solid substance or on a concentrated solution of it.

Phosphoric Acid.

Procedure. — Place 3 or 4 cc. of $(NH_4)_2MoO_4$ solution in a test tube, and add to it not more than half as much of the solution to be tested, having first acidified the latter with HNO_3. Allow the solution to stand, if no precipitate forms at once.

Notes. — 1. The $(NH_4)_2MoO_4$ is used in excess; for the precipitate is less soluble in it than in pure water. Dilute HNO_3 and NH_4NO_3 also diminish its solubility; but HCl and chlorides present in considerable quantity render the test less delicate. In alkaline solution the precipitate does not form.

2. The yellow precipitate is ammonium phospho-molybdate of complicated and somewhat variable composition (approximately $(NH_4)_3PO_4.12MoO_3$).

Procedure. — Add enough NH_4OH to form one third the bulk of the solution, and then a little magnesia mixture ($MgCl_2$, NH_4Cl, and NH_4OH). Stir with a glass rod and allow the mixture to stand for some hours.

Notes. — 1. The NH_4Cl is added to the reagent to prevent the precipitation of MgO_2H_2.

2. H_3AsO_4 gives a similar precipitate. (See Note 5, page 25.) If present, it is first removed by passing H_2S into the hot acidified solution.

3. The test is only applicable when NH_4OH alone produces no precipitate. If metals precipitated by NH_4OH are present, the $(NH_4)_2MoO_4$ test must be used.

Boric Acid.

Procedure. — Add to the solid substance, obtained if necessary by evaporating the solution, concentrated H_2SO_4 and C_2H_5OH. Warm the mixture, set fire to it, and note whether the borders of the flame are colored green.

Notes. — 1. The color is best seen at the moment when the alcohol is lighted.

2. Copper, if present, must be first removed with H_2S.

3. In the presence of chlorides the test is unreliable; for ethyl chloride, which also tinges the flame green, is formed by their action on the alcohol.

4. If a solution to be tested has to be evaporated, it must first be made alkaline, since H_3BO_3 is volatile with steam.

Procedure. — Acidify the solution *slightly* with HCl, and partly dip a piece of turmeric paper in it, and dry. Note whether the dipped part assumes a red tint.

Note. — If the HCl is not very dilute, it imparts a brownish black color to the turmeric paper, which obscures the H_3BO_3 test.

Oxalic Acid.

Procedure. — If the solution is neutral or alkaline, acidify with $HC_2H_3O_2$, add $CaSO_4$, and allow it to stand. If the solution is acid with HCl or HNO_3, first add a considerable quantity of $NaC_2H_3O_2$, and then add $CaSO_4$.

Notes. — 1. CaC_2O_4 is nearly as insoluble in $HC_2H_3O_2$ as in H_2O. The presence of that acid is necessary to prevent the precipitation of other calcium salts, such as $CaCO_3$, $Ca_3(PO_4)_2$. CaF_2, however, is also insoluble in $HC_2H_3O_2$.

2. Mineral acids dissolve CaC_2O_4. $NaC_2H_3O_2$ neutralizes them with formation of their sodium salt and $HC_2H_3O_2$, and is often employed for this purpose in other cases.

Hydrofluoric Acid.

This is commonly met with only in minerals and metallurgical products.

Procedure. — Mix the dry, finely powdered substance in a platinum crucible or on platinum foil with enough strong H_2SO_4 to make a thin paste. Cover it with a watch glass coated on its convex face with beeswax through which some markings have been made with a pointed piece of wood. Fill the watch glass with cold water, and warm the mixture very gently, taking care not to melt the wax. After half an hour, melt off the wax and examine the glass for etchings.

Notes. — 1. In order to detect small quantities of fluorine, a large excess of H_2SO_4 should be avoided, the watch glass should fit the crucible or foil closely, and considerable time should be allowed. By breathing on the watch glass slight etchings, not otherwise noticeable, are made apparent.

2. The etching is due to the action of HF on the silicate of the glass, SiF_4, a gas, being formed.

3. If the substance tested is not decomposed by H_2SO_4, or if it itself contains SiO_2 or silicate, it is evident that the test, if negative, is not conclusive. Another process, described on page 83, is then followed.

Carbonic Acid.

Procedure. — Cover some of the finely powdered substance in a test tube with a little water; boil to expel the air, and add HCl. If bubbles of gas escape, hold a drop of BaO_2H_2 caught on the end of a glass rod just above the surface of the liquid, and note whether it becomes turbid.

Silicic Acid.

Procedure. — Add HCl to the solution, evaporate it to dryness, and ignite the residue at 125° in a hot closet for an hour or more. Moisten with strong HCl, warm, add water, and heat to boiling. If a residue remains undissolved, transfer it to platinum foil, add carefully one or two drops of HF and a drop of H_2SO_4, and heat until the acid is volatilized.

Notes. — 1. For explanation see note 4, page 73.

2. If the residue consists only of SiO_2, it will completely volatilize on treatment with HF, owing to the formation of gaseous SiF_4. ***In using HF take the greatest care not to get it on the hands nor to breathe it.***

HALOGEN GROUP.

Hydrochloric Acid.

The test relied upon in most analyses for the detection of this acid is simply the formation with $AgNO_3$ of a white precipitate insoluble in HNO_3, other halogens being proved absent by the special tests for them. This method is simpler and far more delicate than to try special tests for chlorine. Such tests have to be resorted to, however, in some cases, when other halogens are present.

Hydrobromic Acid.

Procedure. — Add to the neutral or slightly acid solution enough CS_2 to form a large drop at the bottom of the test tube; then add a few drops of chlorine water, and shake the tube.

Note. — The CS_2 is added to dissolve the liberated bromine, thus making the test more delicate. The color is reddish brown if much bromine is present; yellow if only a little. If care is not taken to avoid an excess of chlorine, the solution will be decolorized, owing to formation of bromine chloride, BrCl. Make sure that the chlorine water used smells strongly of the gas.

Hydriodic Acid.

Procedure. — Make the solution distinctly acid with HCl, add a drop of KNO_2 solution and enough CS_2 to form a large drop at the bottom of the test tube, and shake vigorously.

> *Note.* — The HNO_2 liberates iodine and is itself reduced to NO. Chlorine water (as in the test for HBr) answers equally well in most cases, but is not so suitable for the detection of very small quantities of HI, since if used in excess it oxidizes the liberated iodine, thus destroying its color.

Hydrocyanic Acid.

Procedure. — If the solution is acid, make it alkaline by the addition of NaOH; then add solution of $FeSO_4$ and a few drops of $FeCl_3$. Heat the mixture for a short time, and then acidify with HCl.

> *Notes.* — 1. On the addition of the iron salts a greenish black precipitate of ferrous-ferric hydrate forms, even in the absence of HCN; but this dissolves when HCl is added, the insoluble Prussian blue then becoming visible. If only traces of HCN are present, the liquid simply appears green at first, and a slight blue precipitate separates on long standing.
>
> 2. The reactions in this process are:
>
> $$FeSO_4 + 6KCN = K_4Fe(CN)_6 + K_2SO_4$$
> $$3K_4Fe(CN)_6 + 4FeCl_3 = Fe_4(Fe(CN)_6)_3 + 12KCl.$$

Procedure. — If the solution is acid, make it alkaline with NH_4OH, and add one or two drops of (yellow) $(NH_4)_2S_x$. Heat on the water bath till a drop of the solution no longer reacts with $Pb(C_2H_3O_2)_2$; then acidify with HCl and add a little $FeCl_3$.

> *Note.* — The reaction is:
>
> $$(NH_4)_2S_x + (x - 1)\ KCN = (NH_4)_2S + (x - 1)\ KCNS.$$

Hydroferrocyanic and Hydroferricyanic Acids.

Procedure. — Add to one portion of the slightly acid solution a few drops of $FeSO_4$, and to another portion a few drops of $FeCl_3$.

Hydrogen Sulphide.

Procedure. — Warm some of the finely powdered substance in a test tube with dilute HCl, insert a piece of $Pb(C_2H_3O_2)_2$ paper in the top of the tube, and if no blackening appears, add some pure powdered zinc; cork the tube loosely, and allow it to stand.

Notes. — 1. Some sulphides (for example, HgS, FeS_2, etc.) are not decomposed by the acid alone. The nascent hydrogen evolved from the zinc reduces these, however, with evolution of H_2S.

2. If sulphide is present in considerable quantity, it is detected in the preparation of the solution for analysis, either by the odor of H_2S, if the substance is dissolved in HCl, or by the separated sulphur, if HNO_3 or aqua regia is used.

ACIDS OF THE HALOGEN GROUP IN THE PRESENCE OF EACH OTHER.

Iodides, cyanides, and sulphides are readily detected by the tests above described, even in the presence of other acids of the group.

Hydrobromic in the Presence of Hydriodic Acid.

Procedure. — Add to the neutral or slightly acid solution CS_2, and then chlorine water little by little, with constant shaking, until the violet color of the iodine disappears.

Note. — All the iodine is set free before any of the bromine. Excess of chlorine oxidizes it to iodic acid, which is colorless; the bromine is then set free and gives a red or yellow color to the CS_2. Excess of chlorine also decolorizes it, as above stated; hence the need of adding the reagent very slowly.

Hydrochloric in the Presence of Hydrobromic and Hydriodic Acids.

Procedure. — Mix the finely powdered substance intimately with dry powdered $K_2Cr_2O_7$; place in a small dry distilling flask, cover with concentrated H_2SO_4, and heat. Cause the vapors to pass into a test tube containing a little dilute NH_4OH.

Notes. — 1. When chlorides are present, deep red vapors of chromium oxychloride, CrO_2Cl_2, are evolved. The corresponding bromine compound is not formed, but free bromine escapes. The reactions in the two cases are:

$$K_2Cr_2O_7 + 4NaCl + 3H_2SO_4 = 2CrO_2Cl_2 + K_2SO_4 + 2Na_2SO_4 + 3H_2O.$$

$$K_2Cr_2O_7 + 6KBr + 7H_2SO_4 = 3Br_2 + Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O.$$

2. NH_4OH reacts with CrO_2Cl_2 with formation of NH_4Cl and $(NH_4)_2CrO_4$, which imparts a yellow color to the liquid. With Br, NH_4Br and NH_4BrO_3 are formed, both of which are colorless.

3. H_2O decomposes CrO_2Cl_2; hence the need of having the apparatus and the salts perfectly dry.

4. Care must be taken that none of the $K_2Cr_2O_7$ is carried over mechanically by frothing or spurting; for this would of course give rise to a yellow coloration on the addition of NH_4OH.

5. The presence of much HI interferes with this test for HCl. It is removed by precipitating with $AgNO_3$, and treating the precipitate with strong NH_4OH, which dissolves AgCl readily and AgI only very slightly. The AgCl is reprecipitated by HNO_3 and boiled or fused with Na_2CO_3; the solution is filtered and evaporated, and the test with $K_2Cr_2O_7$ and H_2SO_4 made in the usual way.

NITRIC ACID GROUP.

Nitric Acid.

Procedure. — Mix the solution to be tested with an equal volume of strong H_2SO_4, cool, and pour a concentrated $FeSO_4$ solution cautiously down the side of the tube, so that the two liquids do not mix; allow it to stand some minutes, if no color appears.

Note. — The H_2SO_4 sets free HNO_3 from the nitrate; the HNO_3 is then reduced to NO by the $FeSO_4$, and the brown ring is due to the formation of a compound of the two substances last named. This compound is decomposed by heat.

Procedure. — Treat a small quantity of the dry substance with a few drops of phenolsulphonic acid, dilute with water, and make alkaline with NH_4OH.

Notes. — 1. Picric acid is produced by the action of HNO_3 on the phenol, and its formation is indicated by the intensely yellow color of its ammonium salt.

2. The test is exceedingly delicate, and serves to detect very minute quantities of HNO_3. It is used, for example, in testing natural waters, these being first evaporated to dryness.

Chloric Acid.

Procedure. — Add strong H_2SO_4 to a little of the solid substance on a watch glass, and heat gently.

Note. — ClO_2, a greenish yellow gas smelling like Cl, is evolved, which colors the H_2SO_4 intensely yellow. The reaction is:

$$3KClO_3 + 2H_2SO_4 = 2KHSO_4 + KClO_4 + 2ClO_2 + H_2O.$$

Procedure. — Ignite the solid substance in a porcelain dish at a low red heat. Dissolve in water and add $AgNO_3$.

Note. — This test is very delicate, but is applicable, of course, only in the absence or after the removal of chlorides.

Nitric in the Presence of Chloric Acid.

Procedure. — Mix the substance in a small porcelain dish with dry Na_2CO_3 and ignite gently for five to ten minutes. Test in the usual way for HNO_3.

Notes. — 1. The presence of $HClO_3$ prevents the reduction of HNO_3 in the $FeSO_4$ test, and gives a brown color to the phenol sulphonic acid; it must therefore be removed.

2. The chlorate is converted to chloride by ignition; the nitrate is unaffected or partially reduced to nitrite, which gives the same reaction with $FeSO_4$. The use of too high a temperature would destroy the nitrate and nitrite.

3. Nitrates except those of the alkali-metals are very easily decomposed by heat; hence the addition of Na_2CO_3.

Nitric in the Presence of Chromic Acid.

Procedure. — Warm the solution with addition of H_2SO_3 till the color becomes a pure green. Add NH_4OH and filter; test the filtrate with H_2SO_4 and $FeSO_4$.

Nitric in the Presence of Hydriodic Acid.

Procedure. — Add Ag_2SO_4 to the solution acidified with H_2SO_4, as long as a precipitate continues to form; filter and test the filtrate for HNO_3.

ORGANIC ACIDS.

Acetic Acid.

Procedure. — Add a mixture of equal volumes of alcohol and strong H_2SO_4 to the solid substance placed in a test tube; heat gently, and note the odor.

Notes. — 1. The alcohol and acetic acid react in the presence of H_2SO_4 with formation of ethyl acetate, $C_2H_5(C_2H_3O_2)$, a volatile liquid with a pleasant ethereal odor.

2. If the mixture is heated too hot, other products (ether, SO_2, etc.) are formed by the action of the H_2SO_4 on the C_2H_5OH, whereby the odor of the ethyl acetate is concealed.

3. Till perfectly familiar with the odor, the student in trying the test should always make a comparative experiment with a pure acetate.

Tartaric Acid.

Procedure. — Evaporate the solution to the volume of a few drops, slightly acidify with $HC_2H_3O_2$, add some $KC_2H_3O_2$ solution, stir with a glass rod, and allow it to stand.

Notes. — 1. The crystalline precipitate is $KHC_4H_4O_6$, potassium acid tartrate, cream of tartar. The test is exceedingly characteristic, for no other potassium salt (except K_2PtCl_6) is nearly so insoluble. It is not very delicate, however, owing to the slight solubility of the precipitate in water; still, if care is taken to have the solution very concentrated, and if time is allowed, it is sufficiently so for most purposes.

2. Addition of C_2H_5OH greatly diminishes the solubility of the precipitate; before adding it, however, it is necessary to make sure that it alone (without $KC_2H_3O_2$) does not give a precipitate with the solution.

3. If the solution contains HCl or HNO_3, this should be removed by evaporating to dryness on the water bath, since strong acids readily dissolve $KHC_4H_4O_6$.

4. If the solution contains potassium salts, the precipitate forms, of course, as soon as the $HC_2H_3O_2$ is added. In preparing the solution to test for tartrates, it is better to boil the substance, if insoluble, with K_2CO_3 than with Na_2CO_3 solution; for potassium salts diminish and sodium salts increase the solubility of $KHC_4H_4O_6$.

Procedure. — Make the solution slightly alkaline with NH_4OH, add $CaCl_2$ in excess, allow it to stand a short time, filter, treat the precipitate in the cold with strong $NaOH$, dilute, filter if not clear, and heat the filtrate to boiling.

Note. — $CaC_4H_4O_6$ is precipitated from neutral or ammoniacal solution by $CaCl_2$. Presence of ammonium salts retards the precipitation. The solubility of the precipitate in cold $NaOH$ and its reprecipitation on boiling are particularly characteristic of tartaric acid.

ANALYSIS IN THE DRY WAY.

GENERAL REMARKS.

The methods so far described make it possible to detect and separate the metals and acids only when in solution. Valuable information in regard to the composition of a material may, however, often be obtained by making a few simple tests directly with the solid substance. Such tests are of value, first, as a preliminary indication of the presence of specific elements or compounds; for the knowledge thus obtained often facilitates the preparation of the solution for analysis, and enables the subsequent analysis in the wet way to be more intelligently carried out. They are of value, secondly, as an independent method of analysis which may replace the more lengthy wet process in cases where information only in regard to the presence or absence of particular elements is desired, or where the facilities of a well-equipped laboratory are not available.

Where a complete analysis in the wet way is to be made, it is usually not worth while to make all the tests described below; for the physical properties of the substance, its behavior towards solvents, and the precipitates produced by the general reagents, indicate in most cases very quickly the nature of the metals present in considerable proportion. The closed tube test should, however, always be made; for it shows at once the presence or absence of organic matter and of water, and in many cases the nature of the acids contained in the substance. Moreover, if any special difficulty is met with in getting the substance into solution, it is always advisable to try all the dry tests before proceeding.

It should be understood, however, that these dry tests, especially when applied to complex substances with negative results are not as delicate nor conclusive as those made in the wet way; also that some of the reactions are readily obtained and correctly interpreted only after considerable experience. The student, therefore, should not at first draw too positive conclusions from the results.

SPECIAL TESTS.

Procedure.— Place a little of the finely powdered substance in a glass tube sealed at one end. Heat gently at first, and then to the highest heat of the flame. Note any change of appearance and any odor. During the heating apply a flame to the mouth of the tube, and insert in it a glowing wood-splinter or a smouldering bit of twine.

Notes.— 1. The important indications furnished by this test are in regard to the presence of (1) organic matter, (2) water, (3) compounds of volatile metals and (4) in regard to the nature of the acid elements of the substance. The characteristic phenomena that may be observed are (1) carbonization, (2) formation of a distillate or sublimate, (3) evolution of a gas, (4) fusion or change of color.

2. Especial attention must be given to determining whether the substance carbonizes; first, because, if organic matter is present it must be destroyed (as described on page 74), before proceeding with the detection of the metals; and secondly, because, if organic matter is not present, the tests for organic acids may be omitted. For a fuller discussion of carbonization see the notes on page 51.

3. As water is used in preparing the solution, its presence must of course be determined by a test made with the original substance. If present, it should always be reported. In order to detect it, keep the upper part of the tube as cool as possible during the first part of the heating, so as to cause it to condense. It may be present in the substance as water of constitution, as in FeO_3H_3 and Na_2HPO_4; as water of crystallization, as in $MgSO_4.7H_2O$; as hygroscopic moisture on the surface; and as water mechanically enclosed within the crystals. Speaking generally, the temperature required for the expulsion of water is lower in the order named.

4. The sublimates which may be obtained and the corresponding indications are:

Black, accompanied by a garlic odor	As
Black, forming minute globules when rubbed	Hg or a compound of it.
Black, becoming red when rubbed	HgS.
Black, accompanied by violet vapors	I.
Reddish brown drops becoming a yellow solid on cooling	S or a persulphide.
Yellow	S or As_2S_3.
White, quite volatile	An NH_4 salt, As_2O_3, HgCl, $HgCl_2$, or an organic acid.
White, difficultly volatile	Sb_2O_3.

From all compounds of NH_4, Hg, and As (except As_2O_5, arsenites, and arseniates) these components volatilize readily and completely. Therefore, if the substance containing them was for the most part insoluble, and was decomposed by fusion, they might escape detection altogether, if the closed tube test were omitted.

5. The gases that may be evolved and the compounds that they indicate are shown in the following table:

Gas:	Known by:	Indicates:
O_2	Inflaming a glowing splinter.	A chlorate, peroxide, or alkali nitrate.
NO_2	Its odor, and brownish-red color.	A nitrate or nitrite.
SO_2	Its odor.	A sulphate, sulphite, or sulphide.
NH_3	Its odor.	An ammonium salt, a cyanide or nitrogenous organic matter.
H_2S	Its odor and by blackening lead acetate paper.	A moist sulphide.
CO	Burning with a blue flame.	An oxalate.
CO_2	Causing turbidity in a drop of BaO_2H_2.	A carbonate, oxalate, or organic matter.
Cl_2; Br_2; I_2	Their odor and color.	A chloride, bromide, or iodide.

6. The substance may undergo a change of color. Some of the indications are as follows:

Original color:	Color while hot:	Color after cooling:	Indication:
White.	Yellow.	White.	Zn.
White.	Yellow.	Pale yellow.	Sn.
White or yellow.	Brownish red.	Deep yellow.	Pb.
White or yellow.	Brownish red.	Pale yellow.	Bi.
Yellow or brown.	Black.	Brownish red.	Fe.
Yellow or red.	Green.	Green.	A chromate.
Pink, green, or blue.	Black.	Black.	Co, Ni, Cu.

7. If the substance fuses without volatilization or expulsion of aqueous vapors, or if it remains in a state of fusion after volatile matters have been expelled, it is probably a compound of an alkali metal. In that case try the color imparted by it to the flame.

Procedure. — Heat some of the dry powder in a small cavity on a piece of charcoal before the reducing flame of the blowpipe. Observe the odor evolved and the nature of the incrustation and of the residue in the cavity.

Notes. — 1. The metals reduced to the metallic state and forming globules are Pb, Ag, Bi, Sb, Cu, and Sn. Bi and Sb are distinguished by their brittleness from the others; Cu is known by its red color. (Au forms a yellow globule.)

2. The characteristic incrustations formed are the following:
White, very volatile, at a distance from the cavity: As.
White, votatile with some difficulty: Sb.
Yellow when hot, white when cold: Zn and Sn.
Yellow both hot and cold: Pb and Bi.
Reddish brown: Cd.
Dark red: Ag.

3. The evolution of a garlic odor indicates As, and of SO_2, a sulphide. If the substance deflagrates, it is probably a chlorate or nitrate.

Procedure. — Make a clear bead by fusing some $NaPO_3$ or $(NH_4)NaHPO_4$ on the loop of a platinum wire, add to it a little of the substance to be tested, and heat it in the oxidizing flame of a Bunsen burner. Observe the color of the bead when both hot and cold. Then heat it in the reducing flame.

Notes. — 1. The color imparted to the bead depends in many cases on whether it is heated in the oxidizing or reducing flame. To obtain an oxidizing action, heat the bead in the edge or at the top of the non-luminous flame of the Bunsen burner. To get a reducing action, cut off the supply of air to the burner enough to produce a small luminous cone in the interior of the flame, and heat the bead in this cone.

2. The following are the characteristic colorations which the cold bead may exhibit: Blue in both flames: Co. Green and in both flames: Cr. Greenish blue in the oxidizing, red and opaque in the reducing flame: Cu. Amethyst red in oxidizing, colorless in the reducing flame: Mn. Brownish red in the oxidizing flame while hot, yellow or colorless when cold: Fe or Ni. Enamel-white after cooling: Ba or Sr; but many other metals produce this same effect, when a considerable amount of the substance containing them is added to the bead.

3. One of the most important indications of the bead test is in regard to silicic acid. If this substance is present, it floats about undissolved in the melted bead as a semi-transparent skeleton. This distinguishes it from all metallic oxides.

4. By the action of heat NH_4NaHPO_4 changes to $NaPO_3$, sodium metaphosphate; and it is far more convenient in practice to make the beads directly with the latter substance, which can be prepared from the former in quantity by ignition. The colors imparted by different metals are due to the formation of double orthophosphates; for example, $MnNaPO_4$, $CoNaPO_4$, etc.

5. Borax, $Na_2B_4O_7$, is sometimes used in place of $NaPO_3$. The colors produced are the same in most cases, but not in all. It is, however, in general less suitable than $NaPO_3$; for it does not show satisfactorily the silicic acid reaction.

Procedure. — Add a few drops of strong H_2SO_4 to some of the finely powdered substance placed in a very small test-tube, and heat gently — enough to cause volatilization of the H_2SO_4.

Note. — For the indications furnished by this test, see the notes on page 54. It is valuable especially as a means of detecting certain volatile acids which may not be shown by the closed-tube test.

Procedure. — Introduce on the loop of a clean platinum wire a little of the substance moistened with H_2SO_4 into the outer edge of the lower part of the Bunsen flame. As soon as the coloration has nearly ceased, moisten the substance on the wire with HCl, and again introduce it into the flame. Observe the flame closely and continuously until the substance is burnt off. If it is colored yellow, look at it through a thick piece of blue cobalt glass.

[Examine the flame by means of a spectroscope, and compare the spectrum as to the position of its lines with the spectra produced by pure compounds of the elements suspected to be present.]

Notes. — 1. The characteristic flame colorations are as follows:

Yellow: Na.
Red: Ca, Sr, (Li).
Violet: K, (Rb, Cs).
Green: Ba, Cu, H_3BO_3, (Tl).

2. By proceeding as here directed elements may often be detected even in the presence of one another by their flame colorations; for the alkali metals first volatilize, leaving behind the alkaline-earth sulphates, which can then be detected by moistening with HCl, since their chlorides are much more volatile than their sulphates. Moreover, the use of blue glass makes it possible to detect potassium in the presence of sodium, for the yellow light caused by the latter metal is thus completely absorbed. It should always be proved, however, by testing with a pure sodium salt, that the blue glass is of sufficient thickness to cut off the sodium light completely.

3. The spectroscope is a valuable aid in qualitative analysis as a means of detecting elements present in such minute quantities that they are not revealed by the ordinary methods, especially in testing the purity of a substance, in examining mineral waters, or any other material of which only a small amount is available, in detecting the rarer elements in minerals, etc. It may also, in special cases, be used with advantage as a substitute for the far more lengthy wet processes; for example, in the analysis of the alkaline-earth group, or of the group of rare earthy metals: it is not, however, usually a satisfactory substitute for these; for a good qualitative analysis should not only establish the presence or absence of the elements, but also determine roughly the relative proportions of those present, a thing which spectrum analysis (in its ordinary form) entirely fails to do. — The elements which give the most characteristic spectra when heated in the flame are Na, K, Li, Rb, Cs, Ba, Sr, Ca, Tl, In.

PREPARATION OF THE SOLUTION.

I. FOR THE ANALYSIS FOR METALS.

Non-Metallic Substances.

Procedure. — Place about one gram of the *finely powdered* substance in a test tube, add considerable water, and heat to boiling. If the substance dissolves completely, test the solution with litmus paper, and use it for the analysis for metals. If in doubt whether anything dissolves, filter a little of the liquid, and cautiously evaporate three or four drops to dryness on a small watch glass. If partial solution takes place, allow the substance to settle out, decant, and boil the residue with a fresh portion of water. If the substance does not now dissolve, add to the water a few drops of HCl, and heat, noting carefully whether effervescence or evolution of any odor occurs; if necessary, add, little by little, more HCl. In case dilute HCl does not effect solution, rinse the residue into a porcelain dish, decant the liquid, and boil for some time with strong HCl. If this does not suffice, add one third the volume of strong HNO_3, and heat again. A residue remaining after continued action of aqua regia must be fused with Na_2CO_3. Mix together the various liquids by which any of the substance has been dissolved. If only dilute HCl has had to be used, dilute the solution and pass in H_2S directly. If much strong HCl or any HNO_3 was necessary, evaporate the solution just to dryness, moisten the residue with a few drops of HCl, add considerable water, heat, and pass in H_2S. For modifications of this procedure in certain special cases, see the following notes 4, 5, and 6.

Notes. — 1. An acid reaction of the aqueous solution may be due to free acids, acid salts of strong acids, or to neutral salts of most metals of the H_2S and $(NH_4)_2S$ groups. An alkaline reaction shows the presence of a soluble hydrate, carbonate, sulphide, phosphate, borate, or cyanide. It is to be noted that the terms "acid salt" and "neutral salt" refer only to the extent of the replacement of the hydrogen of the acid by the metal, and do not show the reaction towards litmus or other indicators. The latter depends on the relative strength of the acid and base. Examples: Na_2CO_3, Na_2S, and even the acid salts, $NaHCO_3$, Na_2HPO_4, react alkaline. $ZnSO_4$, $CuCl_2$, etc., react acid.

2. It is desirable to use as little HCl as possible in dissolving the substance, since otherwise it is necessary to evaporate the solution before passing in H_2S.

3. HCl may cause evolution of CO_2, H_2S, SO_2, HCN, or Cl (from chlorates, chromates, or peroxides), thus indicating the nature of the acid present.

4. HCl may also cause separation of gelatinous silicic acid. When this occurs, and even when it does not, if the substance is a mineral or metallurgical product liable to contain silicate, the solution should be evaporated to dryness, and the residue ignited at 125° in the hot closet for at least an hour; the mass should then be dissolved in a little HCl, water added, the solution filtered, and the analysis proceeded with. This is done to remove the silicic acid, which in the hydrated condition dissolves to a considerable extent in acid, but which is dehydrated and made insoluble by ignition. This could, of course, be accomplished by direct ignition over the lamp; but it is then very difficult to get Al_2O_3 and Fe_2O_3 again into solution. If the silicic acid is not removed, it precipitates on the addition of NH_4OH, and may be mistaken for AlO_3H_3.

5. In case the preliminary examination indicates the presence of lead or silver, treat the substance first with HNO_3 instead of with HCl; then decant and use aqua regia if necessary. Or if in any case HCl has been tried, and has been found to leave a white residue resembling $PbCl_2$ or AgCl, treat a fresh portion of the substance with HNO_3.

6. If the preliminary examination shows the presence of organic matter, this must be destroyed before proceeding,

since it interferes with the various tests, particularly with the precipitation of the trivalent metals by NH_4OH. The methods used for destroying it vary with the nature of the substance, and directions cannot be given to cover every case.

a. If the proportion of mineral matter is large, ignite the substance at a low temperature in a porcelain crucible till fully charred; cool, moisten with HNO_3, and ignite again carefully at first, and then strongly. Repeat the addition of HNO_3 and ignition till the carbon is consumed. Boil the residue with a small quantity of strong HCl, dilute, filter, and proceed with the analysis as usual. This method is applicable, for example, to baking powders, which it is often necessary to test for Al. Mercury, ammonium, arsenious and antimonious compounds are volatilized.

b. If the substance is mostly organic, heat it in a porcelain dish on the steam bath for ten or fifteen minutes with a mixture of about equal parts of strong H_2SO_4 and HNO_3, then heat over a lamp till white fumes of H_2SO_4 escape; cool, add HNO_3 and heat again; repeat this process till the H_2SO_4 becomes light colored. Dilute with water, boil to expel SO_2 and filter. This method is suitable for destroying paper, fabrics, foods, etc. The H_2SO_4 solution so obtained may be put directly into a hydrogen generator and tested for As and Sb (page 25); for As and Sb in the higher form of oxidation, to which they are converted by the HNO_3, are not volatile. In using this method bear in mind the insolubility of the sulphates of Ba, Sr, Ca, and Pb.

c. If the substance contains oily or fatty matter, extract this by treating the substance two or three times with ether, and use the residue for analysis. Paints in oil, for example, are conveniently treated in this way.

7. If sulphides are present, and HNO_3 or aqua regia is used for dissolving, sulphur separates in the form of a light spongy mass, often black at first owing to inclosed matter, but becoming yellow on continued boiling. It may be tested by heating on porcelain when it burns with a blue flame and odor of SO_2.

8. When strong acids have been used for dissolving the substance, on evaporating these a white residue insoluble in dilute HCl is sometimes obtained. This may be SiO_2, $PbSO_4$, $CaSO_4$, CaF_2, or H_2SnO_3. If there is reason to think it may be $PbSO_4$, treat it with $(NH_4)C_2H_3O_2$ solution. (See

note 2, *c*, page 76). Test it for $CaSO_4$ or CaF_2, by trying the color it imparts to the flame when moistened with HCl. Test it for Sn before the blowpipe on charcoal.

9. If gelatinous silicic acid separates on treating with HCl, it is impossible to tell whether the substance has been completely decomposed. To determine this, filter, wash the precipitate, and boil it with Na_2CO_3. If it is pure silicic acid, it will entirely dissolve.

10. It is not always advisable to mix the aqueous and acid solutions of the substance as has been directed; for they may precipitate each other. For example, in treating in the usual way a substance composed of Na_2SO_4 and $BaCO_3$, the former salt would dissolve in water, and the latter in dilute HCl, but on mixing the two solutions insoluble $BaSO_4$ would precipitate. In practice, therefore, always mix small portions of the two solutions first. Even where they do not precipitate each other, they are sometimes analyzed separately, in order to learn how the metallic and acid radicals are combined with each other.

11. Substances soluble only in hot water or concentrated acids and separating out on cooling or dilution are to be treated as insoluble.

Procedure. — If any insoluble residue remains after the treatment with acids, wash it thoroughly and try such of the tests and separations described in note 2 below as the appearance of the residue and previous indications warrant. If a residue still remains, dry it, mix it with five or six times its weight of Na_2CO_3, and fuse it, in platinum if reducible metals are known to be absent by the preliminary examination on charcoal or by the tests just tried, otherwise in a covered porcelain crucible. If acids have not acted on the substance, or if they have dissolved only a small part of it, fuse a very finely powdered portion of the original substance instead of that treated with acids. Use enough Na_2CO_3 and a high enough heat to make the mixture fuse to a thin liquid; continue the heating ten or fifteen minutes, or longer if effervescence has not ceased. Boil the fused mass with water till disintegrated, filter and wash the residue till free from Na_2CO_3. Dissolve a small part of it in dilute HNO_3, and test the solution with HCl for Ag (and Pb); dissolve the remainder in dilute HCl. Mix with a small portion of this solution a little of the aqueous solution of the fusion, and make the mixture acid, if it is not already so. If no precipitate forms, reserve one half of the aqueous solution for the tests for acids, and mix the other half with the acid solution of the fusion; acidify if alkaline, evaporate to dryness, and ignite for an hour or more at 125° to render silica insoluble; dissolve in a little HCl, dilute with water, filter, and proceed with the analysis (page 17). If the aqueous and acid solutions precipitate each other on mixing, use only the acid solution for the analysis for metals. For modifications of the method of fluxing applicable in special cases, see notes 7 and 8 below.

Notes. — 1. The important substances insoluble or difficultly soluble in water and acids which may be found in the insoluble residue are: C, S, $BaSO_4$, $SrSO_4$, $CaSO_4$, $PbSO_4$, $PbCl_2$, AgCl, CaF_2, silica and many silicates, and the native or ignited oxides of Al, Cr, Fe, and Sn.

2. It is often advantageous to try special tests for some of these substances and to remove them if present before fusing; first, because fusion may thereby become unnecessary, and secondly, because it can then almost always be made in platinum vessels. These tests, which should be tried when there are indications that the substances tested for are present, are as follows:

a. Heat the residue in a porcelain crucible with free access of air. Carbon (except graphite) and sulphur are hereby consumed, the latter burning with a blue flame and odor of SO_2. If S is present and a residue remains, see if it will not now dissolve in acids.

b. Boil the residue with water. This dissolves out $PbCl_2$.

c. Heat the residue with a strong $NH_4(C_2H_3O_2)$ solution acidified with a few drops of $HC_2H_3O_2$. Filter, and test one portion of the filtrate for H_2SO_4 with $BaCl_2$, another for Pb with an excess of H_2SO_4, and a third for Pb with $(NH_4)_2S$. $PbSO_4$ is dissolved by $NH_4(C_2H_3O_2)$, and is reprecipitated when the solvent is destroyed by addition of H_2SO_4.

d. Warm the residue with water and a lump of KCN; filter, add $(NH_4)_2S$ to the filtrate, filter if a precipitate forms, wash, dissolve the precipitate in hot dilute HNO_3, dilute and add HCl. AgCl is dissolved by KCN, and the Ag is precipitated from that solution by $(NH_4)_2S$. Do not attempt to reprecipitate the AgCl by addition of acids to the KCN solution; for HCN gas, which is exceedingly poisonous, would be evolved.

e. If the residue seems to be nothing but SiO_2, treat it in a platinum crucible with a few cc. of HF, evaporate off the acid and note whether anything remains; if there is still a residue, try to dissolve it in HCl. In using HF, take great care not to get it on the hands nor to inhale the gas.

3. Fusion with Na_2CO_3 decomposes most substances, and is especially useful analytically as a means of bringing insoluble substances into a soluble form. A metathesis takes place; the acid radical of the compound combines with the sodium, and a carbonate of the metal is formed; or, if the carbonate is decomposed by heat, the oxide or the metal itself is obtained. The following are some examples:

$$BaSO_4 + Na_2CO_3 = Na_2SO_4 + BaCO_3.$$
$$Al_2SiO_5 + Na_2CO_3 = Na_2SiO_3 + Al_2O_3 + CO_2.$$
$$4AgCl + 2Na_2CO_3 = 4NaCl + 4Ag + 2CO_2 + O_2.$$

The acid element or radical of the original compound is therefore found in the aqueous, and the metallic element in the acid solution of the fusion.

4. In case a substance is dissolved only partially by acids, it may seem simpler to fuse the original substance with Na_2CO_3 rather than the insoluble residue. This is, however, generally not the case; first, because some substances, especially metallic sulphides and alkaline-earth phosphates, though readily soluble in acids, are only slightly decomposed by Na_2CO_3; secondly, because complete decomposition with Na_2CO_3 is at best often difficult to attain, and therefore the amount of substance treated should be as small as practicable; and thirdly, because volatile metals, especially mercury, would be lost.

5. It is preferable to use platinum where admissible, for two reasons: First, it is much easier to obtain the requisite

high temperature; and secondly, Na_2CO_3 attacks porcelain, so that subsequent tests for aluminum and silica are unreliable. Platinum vessels cannot be used, however, when readily reducible metals (Pb, Ag, Cu, Hg, As, Sb, Bi, Sn), sulphides, or phosphates together with organic matter, are present, as they would then be spoiled through the formation of fusible alloys. Alkali hydrates and nitrates in the fused condition, and any solution evolving chlorine, as aqua regia, also attack them.

6. The first and third reactions of note 3 are examples of cases where the aqueous and acid solutions must not be mixed. The second reaction, a type of case very commonly occurring, admits of it, however. The advantage of adding some of the aqueous solution to that used for the analysis for metals is that certain metals, those whose oxides are soluble in excess of alkali, may pass into the aqueous solution as sodium salts.

7. If the residue insoluble in acids contains stannic oxide, calcium fluoride, alumina, ferric oxide, or chromic iron, these substances would be little affected by fusion with Na_2CO_3, and would be found still insoluble in acids. Therefore, when the preliminary examination indicates the presence of any of these, it is better to make use of other fluxes than Na_2CO_3. The choice depends on the considerations set forth in the following note.

8. *Fluxes.* — Four kinds of fluxes may be distinguished: 1. Alkaline fluxes, such as Na_2CO_3, which are suited for the decomposition of most *salts*, and especially of *silicates*. 2. Acid fluxes, especially $KHSO_4$, which is used for the conversion of *basic oxides* (Al_2O_3 and aluminates, Fe_2O_3, Cr_2O_3, etc.) into soluble sulphates. The silica of a silicate is thereby separated in insoluble form. In using this flux take care not to continue the heating till the sulphuric acid ceases to come off; for insoluble basic sulphates then result. 3. Oxidizing fluxes, for example mixtures of Na_2CO_3 with $NaNO_3$ or $KClO_3$, which serve to convert compounds of *acid forming metals* (like Cr, As) into soluble salts of their acids. Insoluble native sulphides are also best treated in this way. 4. Reducing fluxes, for example a mixture of Na_2CO_3 and KCN, which are sometimes useful in separating *reducible metals* from their oxides,

as Sn from native SnO_2. — Chromic iron is decomposed by fusing first with $KHSO_4$, and then treating the undecomposed residue with Na_2CO_3 and $NaNO_3$.

Procedure. — To test for alkali metals in a silicate not acted on by acids, decompose the mineral without the use of alkaline carbonates as follows: Mix one part of the very finely powdered substance with six parts of pure $CaCO_3$ and one part of NH_4Cl, and heat the mixture to bright redness in a covered platinum crucible for half an hour, taking care to heat only the bottom of the crucible. Heat the sintered mass with water for half an hour, filter, add to the filtrate a little NH_4OH, and $(NH_4)_2CO_3$ in slight excess; heat to boiling, filter, and remove ammonium salts from the filtrate and test for K and Na as directed on page 48.

Notes. — 1. Alkali silicates, though soluble in water when alone present, are often not dissolved out of double silicates even by acids. Hence the need of a special test as above described.

2. $CaCO_3$ decomposes the silicate in the same way as Na_2CO_3. The NH_4Cl serves to convert the alkali metals to chlorides. The aqueous extract obtained contains the hydrates and chlorides of Ca, K, and Na. The $(NH_4)_2CO_3$ is added to precipitate the Ca.

3. If the whole crucible is heated to bright redness the alkali chlorides are lost by volatilization. The heat used should be sufficient to make the mixture sinter, but not fuse.

Metals and Alloys.

Procedure. — Cut the alloy into small pieces, or hammer it out so as to expose as great a surface as possible. Heat about one gram of it with 25 cc. of strong HNO_3 (1.2 spec. grav.) as long as any action continues. If metal protected from further action of the solvent by the products of the reaction still remains, pour off the acid, treat the residue with water, and then with a fresh portion of strong HNO_3.

If complete solution takes place, dilute with water and add HCl. If a precipitate ($PbCl_2$ or AgCl) forms, filter it off and examine it in the usual manner for Pb and Ag. Evaporate the filtrate, or the solution in which HCl produces no precipitate, to dryness; moisten the residue with HCl, and evaporate once again just to dryness to expel the HNO_3. Dissolve the residue in water with addition of a little HCl, pass in H_2S, and proceed with the analysis as usual, except that the $(NH_4)_2S_x$ treatment of the H_2S precipitate may be omitted. (See note 2.)

If a white residue remains, dilute the HNO_3 solution with water, filter, and treat the filtrate as directed in the last paragraph. Wash the residue with hot water till free from acid, transfer it to a porcelain dish, and heat it with a considerable quantity of $(NH_4)_2S_x$. The white residue should entirely dissolve; if a small black residue consisting of sulphides of metals of the copper group remains, filter it off. Test this $(NH_4)_2S_x$ solution for As, Sb, and Sn in the usual manner. In case the white residue left by the HNO_3 is large, and it is found to be very difficult to get it into solution in $(NH_4)_2S_x$, treat a fresh portion of the alloy with aqua regia, and proceed with this solution as with the HNO_3 solution, except that the separation with $(NH_4)_2S_x$ and the analysis of the tin group must in this case be carried out.

Notes. — 1. The nitrates formed in dissolving the alloy, though readily soluble in water, are very little soluble in HNO_3; they may therefore precipitate on the surface of the metal, and prevent further action of the acid.

2. If the alloy is completely soluble in HNO_3, Sn is absent, and not more than a trace of Sb can be present. It is then unnecessary to treat the H_2S precipitate with $(NH_4)_2S_x$; for of the metals of the tin group only As and a trace of Sb can be present, and these are best detected by placing some of the solution from which the HNO_3 has been removed by evaporation in a generator with zinc and HCl. If present, Sb and Sn are oxidized by HNO_3 to the white compounds, metastannic acid (H_2SnO_3) and antimony oxide (Sb_2O_3, Sb_2O_4, or

Sb_2O_5, according to the strength of the acid and temperature). Traces of the latter dissolve in HNO_3.

3. If the alloy contains at the same time P or As, these elements are also found in the white residue in the form of $Sn_3(PO_4)_4$ and $Sn_3(AsO_4)_4$ respectively.

4. In order to detect P in an alloy completely soluble in HNO_3, it is only necessary to add some of the solution to an excess of $(NH_4)_2MoO_4$. To detect it in the white residue, acidify some of the $(NH_4)_2S_x$ solution of the latter with HNO_3, filter out the precipitate, and add the filtrate to an excess of $(NH_4)_2MoO_4$ solution.

5. In the analysis of an alloy all the operations serving for the detection or removal of Cr, Ba, Sr, and Ca are omitted, since these metals are never present. Moreover, K and Na need be tested for only when the alloy decomposes hot water.

6. A black residue consisting of C or Si may remain on treating the alloy with HNO_3. C is found principally in alloys containing Fe, and Si in the newer alloys of Al.

7. An insoluble residue may also consist of the rare metals Au and Pt. They dissolve in aqua regia.

2. FOR THE ANALYSIS FOR ACIDS.

Salts and Industrial Products.

Procedure. — If the substance is *soluble* in water, and only alkaline-earth and alkali metals are present, dissolve about one gram, and use this aqueous solution for the various tests; if, however, other metals are present, add Na_2CO_3 to the solution as long as a precipitate continues to form. If the substance is *insoluble* and metals *not precipitated* by H_2S are present, boil a gram of the finely powdered substance with 10 cc. of strong Na_2CO_3 solution for ten or fifteen minutes, replacing the water which evaporates. Filter off the precipitate or residue, and make half of the filtrate slightly acid with HNO_3. (If a precipitate forms when the solution is neutral, filter it off.) Boil this solution for two or three minutes to expel the CO_2, and use it for the $BaCl_2$ and $AgNO_3$ tests, and for those special tests which may be made in the presence of free HNO_3. Acidify fresh portions of the Na_2CO_3 solution with $HC_2H_3O_2$ for the oxalic (and tartaric) acid test, and with H_2SO_4 for the nitric acid test. If the substance is *insoluble*, and only metals *precipitated* by H_2S are present, suspend a gram of the finely powdered substance in water, saturate with H_2S, heat to boiling, and filter; boil the filtrate till the H_2S is completely expelled, and use it for the $BaCl_2$ and $AgNO_3$ tests and for the various special tests. If not already detected or proved absent, test the original substance for H_2S and H_2CO_3.

Notes. — 1. All metals except arsenic and the alkalies are precipitated from solution by Na_2CO_3 in the form either of carbonate, basic carbonate, or hydrate. Boiling with Na_2CO_3 decomposes almost all salts more or less completely, the acid radical going into solution in combination with sodium, and the metal being precipitated as carbonate or hydrate. Many of these carbonates and hydrates dissolve somewhat in the excess of Na_2CO_3 employed, and they are then precipitated when the alkali is nearly neutralized.

2. The removal of the metals by Na_2CO_3 is necessary; for otherwise the solution cannot be made alkaline, for example with NH_4OH, without the production of a precipitate; moreover, their presence interferes in other ways with some of the special tests.

3. The Na_2CO_3 must be completely neutralized and the CO_2 expelled before testing with $BaCl_2$ and $AgNO_3$; otherwise $BaCO_3$ and Ag_2CO_3 will precipitate.

4. The removal of the metals with H_2S where possible has the advantages that it is more complete than that with Na_2CO_3, and that no additional salts or acids are introduced into the solution. In the presence of chlorates it is inapplicable; for the H_2S is then oxidized, and the tests for $HClO_3$, HCl, and H_2SO_4 are valueless; in the presence of nitrate the test for H_2SO_4 is unreliable.

Minerals and Metallurgical Products.

Procedure. — Try the special tests for H_2S and H_2CO_3 with a portion of the finely powdered dry substance. Boil another portion with HNO_3 for two or three minutes, dilute, filter if not entirely dissolved, and test the filtrate for H_3PO_4 with $(NH_4)_2MoO_4$, and for HCl with $AgNO_3$.

Test for H_2SO_4, *if sulphides are absent*, by adding $BaCl_2$ to some of the HNO_3 solution; if the substance is not completely soluble in HNO_3, test also the aqueous solution obtained from the fusion of the insoluble residue in preparing for the analysis for metals (page 76) by acidifying with HCl and adding $BaCl_2$. *If sulphides are present*, boil some of the original substance with strong Na_2CO_3 solution for some minutes, dilute, filter, acidify with HCl, and add $BaCl_2$.

The presence or absence of H_2SiO_3 has been already determined in the preliminary examination by the $NaPO_3$ bead test, or in the course of the analysis for metals.

Test for HF (with H_2SO_4) and for H_3BO_3 (with H_2SO_4 and C_2H_5OH), *if silicates are absent*, with separate portions of the original substance. To test for these acids, *if silicates are present*, fuse at least a gram of the substance with four or five parts of Na_2CO_3, boil the fused mass with water, and filter. Slightly acidify a little of the filtrate with HCl, and test it for H_3BO_3 with turmeric paper; evaporate half of the remaining filtrate to dryness, and test for H_3BO_3 with H_2SO_4 and C_2H_5OH. Acidify the other half of the filtrate with $HC_2H_3O_2$, allow it to stand, filter off the precipitate, add $CaCl_2$, allow the liquid to stand, collect the precipitate on a filter, and test it in the usual manner for HF.

Notes. — 1. Boiling with Na_2CO_3 fails to decompose many insoluble minerals, slags, etc. Moreover, it is necessary to test these substances for only a comparatively small number of acids; namely, for H_2S, H_2CO_3, H_2SiO_3, H_2SO_4, H_3PO_4, H_3BO_3, HF, and HCl; for the other acids do not occur in them, or occur very rarely. For these reasons a different method of treatment has been given.

2. H_2S and H_2CO_3, if present, are usually detected at the beginning of the analysis on treating the substance with acids. It is only for traces that it is sometimes necessary to test more carefully here.

3. Many phosphates are decomposed very incompletely by

boiling, and even by fusing, with Na_2CO_3; but they all dissolve without difficulty in HNO_3, and are therefore best tested for in this solution.

4. All chlorides except AgCl can also be tested for in the HNO_3 solution. If Ag has been found among the metals, the solution obtained by boiling or fusing with Na_2CO_3 must also be tested for HCl.

5. Sulphides are partially oxidized to sulphates both by boiling with HNO_3 and by fusing with Na_2CO_3. Therefore the substance is boiled with Na_2CO_3, or, if completely soluble, a HCl solution of it may be prepared, in order to test for H_2SO_4 in the presence of H_2S.

6. In the presence of silicates the tests for H_3BO_3 and HF, if made with the original substance, would be unreliable, because the mineral may not be decomposed by H_2SO_4; and in the case of HF, also because this acid, if set free, may be entirely converted to SiF_4 by the silica of the mineral.

7. By fusing such a mineral, Na_2SiO_3, $NaBO_2$, and NaF are obtained in solution. Silicic acid is precipitated on acidifying with $HC_2H_3O_2$, and CaF_2 on the addition of $CaCl_2$.

APPENDIX.

PREPARATION OF REAGENTS.

ACIDS.

Acetic: sp. gr. 1.044; mix one part of the glacial acid with 2½ parts of water.

Aqua regia: mix 1 part HNO_3 with three parts of concentrated HCl.

Hydrochloric, concentrated: sp. gr. 1.12.

Hydrochloric, dilute: mix one part of the concentrated acid with 4 parts of water.

Hydrochloroplatinic: 100 grams $H_2PtCl_6.6H_2O$ to the liter.

Hydrogen sulphide: saturated solution.

Phenolsulphonic: dissolve 150 grams of phenol in 600 grams of concentrated H_2SO_4.

Sulphuric, concentrated: sp. gr. 1.84.

Sulphuric, dilute: mix 1 part of the concentrated acid with 4 parts of water.

Sulphurous: saturated solution.

AMMONIUM SALTS.

Acetate: add 1000 cc. NH_4OH (sp. gr. 0.90) to 1250 cc. glacial acetic acid.

Carbonate: dissolve 250 grams in a liter of water and add 100 cc. NH_4OH (sp. gr. 0.90.)

Chloride: 100 grams to the liter.

Hydroxide: sp. gr. 0.96; mix 1 part NH_4OH (sp. gr. 0.90) with 2 parts water.

Molybdate: mix 100 grams MoO_3 with 400 cc. cold distilled water and add 80 cc. of ammonia (0.90 sp. gr.). Filter, and pour this solution with constant stirring into a mixture of 300 cc. HNO_3 (1.42 sp. gr.) and 700 cc. water.

Oxalate: 40 grams $(NH_4)_2C_2O_4.2H_2O$ to the liter.

Sulphide (colorless): saturate 1500 cc. NH_4OH (sp. gr. 0.90) with H_2S; then add 1000 cc. NH_4OH (sp. gr. 0.90) and 2000 cc. of water.

Persulphide (yellow): add 50–75 grams of sulphur to colorless $(NH_4)_2S$.

Sulphate: 250 grams to the liter.

BARIUM SALTS.

Chloride: 20 grams $BaCl_2.2H_2O$ to the liter.

Hydroxide: 50 grams $BaO_2H_2.8H_2O$ to the liter.

CALCIUM chloride: 100 grams $CaCl_2.6H_2O$ to the liter.

FERRIC chloride: 100 grams $FeCl_3$ to the liter.

FERROUS sulphate: dissolve 200 grams $FeSO_4.7H_2O$ in a liter of water; place scraps of iron in the solution, and add a few drops of H_2SO_4 from time to time.

LEAD acetate: 100 grams $Pb(C_2H_3O_2)_2.3H_2O$ to the liter.

MAGNESIUM ammonium chloride: dissolve 90 grams $MgCl_2.6H_2O$ and 240 grams NH_4Cl in a liter of water, and add 50 cc. NH_4OH (sp. gr. 0.90) to the solution.

MERCURIC chloride: 50 grams to the liter.

POTASSIUM SALTS.

Acetate: saturated solution.

Chromate: 100 grams to the liter.

Ferricyanide: 10 grams to the liter.

Ferrocyanide: 15 grams to the liter.

Nitrite: 500 grams to the liter.

Sulphocyanate: 100 grams to the liter.

SILVER SALTS.

Nitrate: 25 grams to the liter.

Sulphate: saturated solution.

SODIUM SALTS.

Acetate: saturated solution.

Carbonate: 150 grams of the anhydrous salt to the liter.

Hydroxide: 100 grams (Solvay) NaOH to the liter.

Hypochlorite: add 500 grams of bleaching powder and 245 grams of anhydrous Na_2CO_3 to 4000 cc. of water; allow the precipitate to settle and decant the solution.

Phosphate: 100 grams $Na_2HPO_4.12H_2O$ to the liter.

Sulphide: saturate a 10 per cent. NaOH solution with H_2S, and dissolve 50 grams of sulphur in 1 liter of the solution.

STANNOUS chloride: heat an excess of granulated tin with concentrated HCl, adding scrap platinum to facilitate the solution. Dilute with an equal volume of water, and keep the solution in well-stoppered bottles containing metallic tin.

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